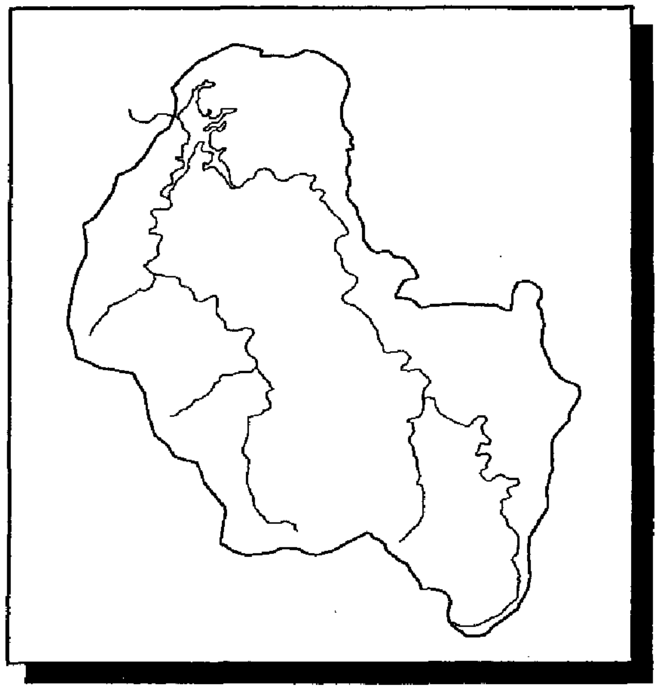
TOTAL MAXIMUM DAILY LOAD AND IMPLEMENTATION PLAN FOR MERCURY ARIVACA LAKE, ARIZONA



Arizona Department of Environmental Quality
U.S. Environmental Protection Agency, Region 9
Tetra Tech, Inc.

October 15, 1999

Acknowledgments

This TMDL was developed through the cooperative efforts of Arizona Department of Environmental Quality (ADEQ) and U.S. Environmental Protection Agency (EPA) based on a study prepared by Tetra Tech, Inc. Dr. Jonathan B. Butcher, Eric Thirolle, and Dr. Curtis W. Pollman of Tetra Tech, Inc. completed the study for U.S. EPA under Contract 68-C7-0018. Additional support was provided by Dr. Reed Harris of Tetra Tech, Gregg Olson, John Hillenbrand, David Smith, and Peter Kozelka of U.S. EPA, Sam Rector and Frank Metzler of the Arizona Department of Environmental Quality, and staff from the United States Forest Service, among others. Field work and sampling to support this TMDL study were carried out by Gregg Olson and John Hillenbrand of U.S. EPA Region 9 with assistance from Sam Rector of ADEQ and staff from Arizona Department of Game and Fish. We wish to thank the Electric Power Research Institute (EPRI) for permission to use the Dynamic Mercury Cycling Model in this study.

TOTAL MAXIMUM DAILY LOAD AND IMPLEMENTATION PLAN FOR MERCURY IN ARIVACA LAKE, ARIZONA

Contents

Tables

Figures

Executive Summary

The Arizona Department of Environmental Quality (ADEQ) has identified Arivaca Lake as not supporting its designated uses due to the presence of fish tissue concentrations of mercury in excess of Fish Consumption Guidelines. Ambient water quality criteria for concentrations of mercury in water have not been exceeded; however, the physical and chemical characteristics of this lake lead to a situation in which mercury readily builds up in fish tissue to levels that present a risk to human health. Because Arivaca Lake does not support its designated uses, ADEQ and U.S. Environmental Protection Agency (EPA) Region 9 have developed a Total Maximum Daily Load (TMDL) for mercury loading to the lake. The TMDL is a mechanism established in the Clean Water Act for situations in which water quality impairment cannot be mitigated by imposition of technology-based effluent limits on permitted point sources. ADEQ included Arivaca Lake on its Clean Water Act Section 303(d) list of waters needing TMDLs beginnning in 1996.

Pursuant to a consent decree entered to settle a TMDL lawsuit (*Defenders of Wildlife v. Browner*, consent decree approved April 22, 1997), EPA is required to ensure that a TMDL is established for all waters identified on Arizona's 1996 Section 303(d) list for mercury. Final TMDLs are required to be established for the first two listed waters by October 22, 1999. Establishment of TMDLs for Arivaca Lake and Pena Blanca Lake will meet this requirement.

The TMDL consists of allocation of the available loading capacity of the lake (the maximum rate of loading that would be consistent with achieving designated uses) to point sources, nonpoint sources, and a margin of safety. This TMDL analysis estimates that the loading capacity of Arivaca Lake is approximately 155 grams of mercury per year. Within the Arivaca Lake watershed there are no permitted point sources of mercury discharge. A dump site with elevated levels of mercury is, however, located at the head of the watershed, though this site does not appear to currently be a major contributor of mercury to the lake. In addition, there are nonpoint or diffuse loads of mercury from naturally occurring background in local rocks, atmospheric deposition, and other sources. This TMDL analysis indicates that approximately a 38 percent reduction in background watershed loading will be needed to reduce mercury loading into the lake to a level sufficient to meet the Fish Consumption Guidelines within 10 years, with a significant unallocated reserve on the loading capacity.

Upon approval by EPA, the State is required to incorporate the TMDL into the State Water Quality Management Plan (WQMP). Although it is not a required component of a TMDL, States are required to identify implementation measures in the WQMP which are necessary to implement the TMDL. Therefore, this document also includes a proposed implementation plan to address mercury loading to Arivaca Lake. The plan includes provisions to 1) conduct a followup watershed survey to identify any previously undetected mercury loading sources, 2) initiate remedial actions if any previously undetected sources are identified, 3) implement erosion control best management practices if no previously undetected sources are identified, and 4) monitor fish tissue mercury levels in order to review and, if necessary, revise the TMDL in the future.

Glossary

Acute toxicity. A stimulus severe enough to rapidly induce a toxic effect; in aquatic toxicity tests, an effect observed within 96 hours or less is considered acute.

Aerobic. Environmental condition characterized by the presence of dissolved oxygen; used to describe chemical or biological processes that occur in the presence of oxygen.

Algae. Any organisms of a group of chiefly aquatic microscopic nonvascular plants; most algae have chlorophyll as the primary pigment for carbon fixation.

Anaerobic. Environmental condition characterized by the absence of dissolved oxygen; used to describe chemical or biological processes that occur in the absence of oxygen.

Anoxic. Aquatic environmental conditions containing zero or minimal dissolved oxygen.

Benthic. Refers to material, especially sediment, at the bottom of an aquatic ecosystem.

Benthic organisms. Organisms living in, or on, bottom substrates in an aquatic ecosystem.

Bioaccumulation. The process by which a contaminant accumulates in the tissues of an organism.

Chronic toxicity. Toxic impacts that occur over relatively long periods of time, often one-tenth of the life span or more. Chronic effects may include mortality, reduced growth, or reduced reproduction.

Cinnabar. A compound of sulfide and mercury (HgS), also known as red mercuric sulfide, which is the primary naturally occurring ore of mercury.

Designated uses. Those beneficial uses of a waterbody identified in state water quality standards that must be achieved and maintained as required under the Clean Water Act.

Epilimnion. The surface water layer overlying the thermocline of a lake. This water layer is in direct contact with the atmosphere.

Eutrophication. Nutrient enrichment of a waterbody leading to accelerated biological productivity (growth of algae and weeds) and an accumulation of algal biomass.

Evapotranspiration. Water loss from the land surface by the combined effects of direct evaporation and transpiration by plants.

Hg. Chemical symbol for mercury.

Hydrophobic. A compound that lacks affinity for water and thus tends to have low solubility in water.

Hypolimnion. The bottom water layer underlying the thermocline of a lake. This layer is isolated from direct contact with the atmosphere.

Lipophilic. A compound that has a high affinity for lipids (fats and oils) and is thus prone to be stored in body tissues.

Load Allocation. The portion of a receiving water's loading capacity that is attributed either to one of its existing or future nonpoint sources of pollution or to natural background sources.

Loading capacity. The amount of contaminant load (expressed as mass per unit time) that can be loaded to a waterbody without exceeding water quality standards or criteria.

Macrophytes. Macroscopic, multicellular forms of aquatic vegetation, including macroalgae and aquatic vascular plants.

Margin of Safety. A required component of the TMDL that accounts for uncertainty in the relationship between the pollutant loads and the quality of the receiving waterbody.

Metalimnion. The water stratum between the epilimnion and hypolimnion containing the thermocline.

Methylation. The process of adding a methyl group (CH_3) to a compound, often occurring as a result of bacterial activity under anaerobic conditions.

Methylmercury (MeHg). A compound formed from a mercury ion and a methyl molecule, CH_3Hg, usually by bacterial activity. Methylmercury exhibits chemical behavior of an organic compound and is the form of mercury most likely to be taken up and retained by organisms.

Morphometry. The shape, size, area, and volumetric characteristics of a waterbody.

Nonpoint source pollution. Pollution that is not released through pipes but rather originates from multiple sources over a relatively large area.

Oligotrophic. Waterbodies characterized by low rates of internal production, usually due to the presence of low levels of nutrients to support algal growth.

pH. A measure of acidity and alkalinity of a solution that is a number on a scale on which the value of 7 represents neutrality and lower numbers indicate increasing acidity. pH is equivalent to the negative logarithm of hydrogen ion activity.

Photodegradation. Degradation of compounds by light energy.

Phytoplankton. Free-floating algae.

Piscivorous. Fish-eating.

Potential Evapotranspiration. An estimate of the evapotranspiration that would occur in response to available solar energy if water supply was not limiting.

Redox potential. A measure of the energy available for oxidation and reduction reactions, represented as the negative logarithm of electron activity in a solution.

Stratification (of waterbody). Formation of water layers with distinct physical and chemical properties that inhibit vertical mixing. Most commonly, thermal stratification occurs when warmer surface water overlies colder bottom water.

Tailings. Residue of raw material or waste separated out during the processing of mineral ores.

Thermocline. A lake water layer separating warmer surface waters from colder bottom waters, correctly defined as the plane of maximum rate of decrease of temperature with respect to depth.

Total Maximum Daily Load (TMDL). The sum of the individual wasteload allocations for point sources, load allocations for nonpoint sources and natural background, and a margin of safety as specified in the Clean Water Act. The TMDL must be less than or equal to the loading capacity and can be expressed in terms of mass per time, toxicity, or other appropriate measures that relate to a state's water quality standards.

Trophic level. One of the hierarchical strata of a food web characterized by organisms that are the same number of steps removed from the primary producers (such as photosynthetic algae). Animals that consume other animals are at higher trophic levels. Certain pollutants such as methylmercury tend to accumulate at higher concentrations in animals at higher trophic levels.

Wasteload allocation. The portion of a receiving water's loading capacity that is allocated to one of its existing or future permitted point sources of pollution.

Watershed. The entire upstream land area that drains to a given waterbody.

1. Background

1.1 Description of TMDL Process

High-quality water is an extremely valuable commodity in Arizona. Water quality standards are established to protect the designated uses of Arizona's waters. When states and local communities identify problems in meeting water quality standards a Total Maximum Daily Load (TMDL) can be part of a plan to fix the water quality problems. The purpose of this TMDL is to provide an estimate of pollutant loading reductions needed to restore the beneficial uses of Arivaca Lake and to guide the implementation of control actions needed to achieve these reductions.

Section 303(d) of the Clean Water Act (CWA) requires states to identify the waters for which the effluent limitations required under the National Pollutant Discharge Elimination System (NPDES) or any other enforceable limits are not stringent enough to meet any water quality standard adopted for such waters. The states must also rank these impaired waterbodies by priority, taking into account the severity of the pollution and the uses to be made of the waters. Lists of prioritized impaired waterbodies are known as the "303(d) lists" and must be submitted to EPA every two years.

A TMDL represents the total loading rate of a pollutant that can be discharged to a waterbody and still meet the applicable water quality standards. The TMDL can be expressed as the total mass or quantity of a pollutant that can enter the waterbody within a unit of time. In most cases, the TMDL determines the allowable loading capacity for a constituent and divides it among the various contributors in the watershed as waste load (i.e., point source discharge) and load (i.e., nonpoint source) allocations. The TMDL also accounts for natural background sources and provides a margin of safety. For some nonpoint sources it might not be feasible or useful to derive an allocation in mass per time units. In such cases, a percent reduction in pollutant discharge may be proposed.

TMDLs developed for Arizona include specific elements needed to comply with federal requirements:

1. **Plan to meet State Water Quality Standards:** The TMDL includes a study and a plan for the specific water and pollutants that must be addressed to ensure that applicable water quality standards are attained.

2. **Describe quantified water quality goals, targets, or endpoints:** The TMDL must establish numeric endpoints for the water quality standards, including beneficial uses to be protected, as a result of implementing the TMDL. This often requires an interpretation that clearly describes the linkage(s) between factors impacting water quality standards.

3. **Analyze/account for all sources of pollutants:** All significant pollutant sources are described, including the magnitude and location of sources.

4. **Identify pollution reduction goals:** The TMDL plan includes pollutant reduction targets for all point and nonpoint sources of pollution.

5. **Describe the linkage between water quality endpoints and pollutants of concern:** The TMDL must explain the relationship between the numeric targets and the pollutants of concern. That is, do the recommended pollutant load allocations exceed the loading capacity of the receiving water?

6. **Develop margin of safety that considers uncertainties, seasonal variations, and critical conditions:** The TMDL must describe how any uncertainties regarding the ability of the plan to meet water quality standards that have been addressed. The plan must consider these issues in its recommended pollution reduction targets.

7. **Include an appropriate level of public involvement in the TMDL process:** This is usually achieved by publishing public notice of the TMDL, circulating the TMDL for public comment, and holding public meetings in local communities. Public involvement must be documented in the state's TMDL submittal to EPA Region 9.

A plan to implement a TMDL is required by federal regulations (40 CFR 130.6) and is being established in this document pursuant to this requirement. EPA expects that this plan will provide a specific process and schedule for achieving pollutant reduction targets. A monitoring plan should also be included, especially where management actions will be phased in over time and to assess the validity of the pollutant reduction goals.

2. Problem Statement

2.1 Waterbody Name and Location

Arivaca Lake is a man-made impoundment located in Pima and Santa Cruz counties, Arizona, on Cedar Canyon in the Santa Cruz River watershed (HUC 15050304). The lake lies in southern Arizona, northwest of Nogales near the Mexican border and 71 miles south-southwest of Tucson, and is within the boundaries of the Coronado National Forest (Figure 1). Arivaca Lake was impounded in 1970. The Arizona Game and Fish Department (AZGF) owns the lake.

Information on the morphometry of Arivaca Lake was obtained from area-capacity curves and an as-built blueprint provided by AZGF. This shows the spillway elevation at 120 feet above an undefined local datum; the spillway elevation is approximately 3,800 feet MSL. At full pool, the lake has a surface area of 89 acres, a volume of 1037.37 acre-feet, a maximum as-built depth of 25 feet, and an average depth of 11.7 feet. Depth-area-capacity information is summarized in Figure 2, including elevations up to the top of the dam, which is 15 feet above the spillway elevation. Releases from the lake are not managed and occur only when pool level reaches the spillway crest.

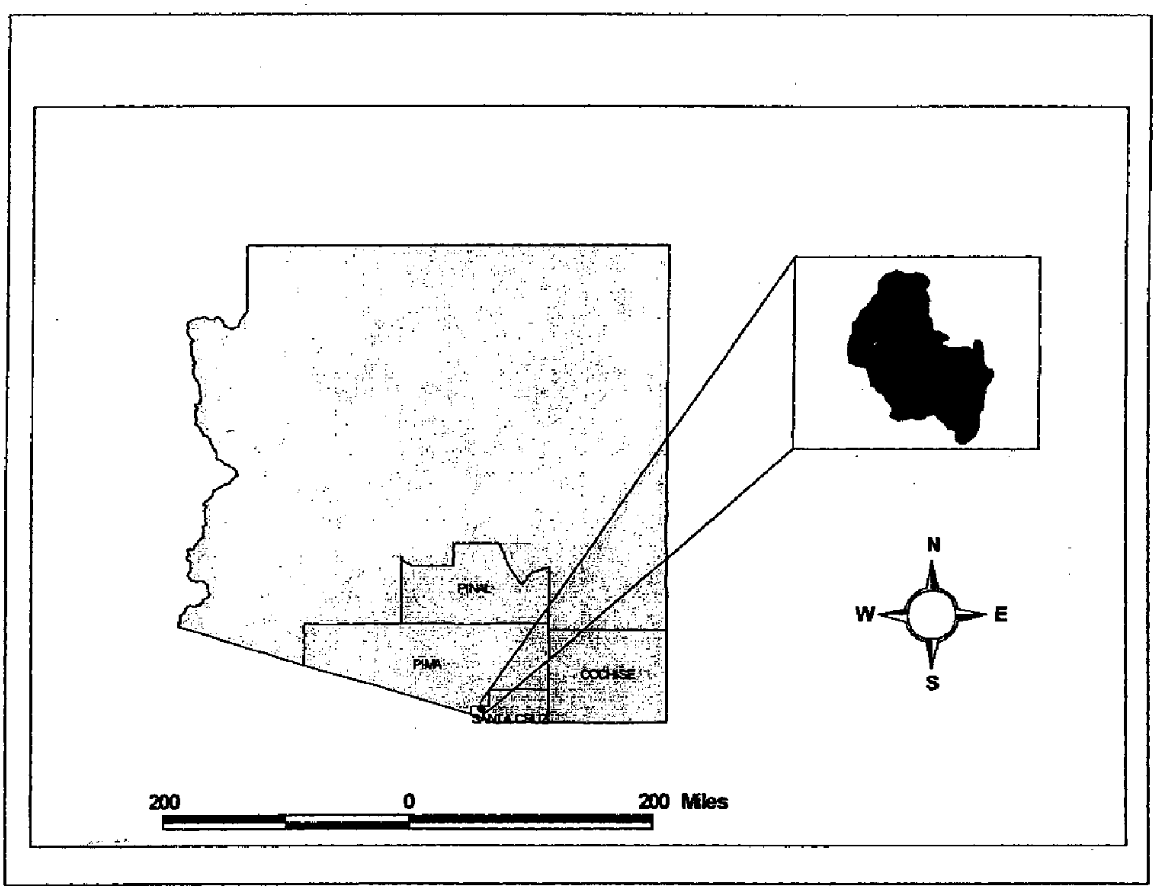


Figure 1. Location Map for Arivaca Lake Watershed, Arizona

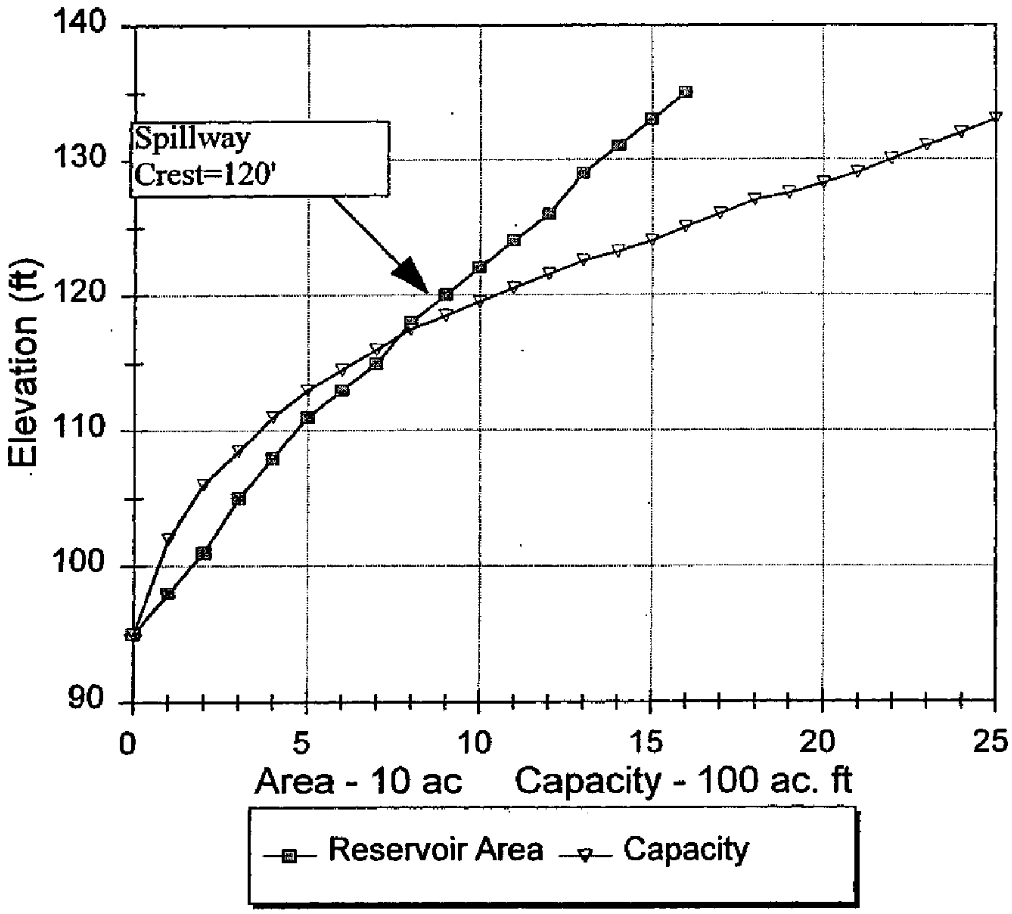


Figure 2. Depth-Area-Capacity Curves for Arivaca Lake

Since impoundment, the lake has lost an unknown fraction of its volume to sedimentation. A study of nearby Peña Blanca Lake in 1973 (NFS, 1973) estimated the loss of capacity to sedimentation at 8 acre-ft/yr. This rate of filling would have reduced that lake's volume by about 15 percent over 30 years; however, improved management practices since 1973 may have reduced sedimentation. No recent data on morphometry of Arivaca Lake has been obtained; however, depths recorded during 1998 EPA sampling do suggest that significant filling might have occurred in some parts of the lake. Lacking quantitative data, the influence of potentially reduced lake volume has not been included in this TMDL analysis.

Arivaca Lake experiences nuisance growths of aquatic macrophytes, as do many other Arizona lakes; however, this seems to be less of a problem in Arivaca than in Peña Blanca Lake. AZGF conducts restoration activities at Arivaca to improve fishing and recreational opportunities through removal of aquatic macrophytes by mechanical harvesting. AZGF records show that from 1 to 20 acres per year of macrophytes were harvested between 1985 and 1994, but no harvesting has occurred since 1994. Notes from a May 1995 survey note that high water conditions and an algae bloom had reduced light penetration and reduced the regrowth of aquatic macrophytes (Mitchell, 1995b).

Arivaca Lake is a popular fishing destination and is known as a source of trophy-size largemouth bass. AZGF manages the lake as a year-round self-sustained warm water fishery, and has stocked largemouth bass of several strains. AZGF conducted a creel survey in Arivaca Lake in 1994 and an aquatic wildlife survey in 1995 (Mitchell, 1995a, 1995b). Sampling by electrofishing found that Arivaca supports a healthy fish community dominated by largemouth bass, bluegill sunfish, and redear sunfish, with lesser numbers of channel catfish and green sunfish.

2.2 Water Quality and 303(d) Status

The applicable water quality standards for Arivaca Lake are determined by the uses designated in state regulations. Arizona has designated the uses for Arivaca Lake as Aquatic and Wildlife (warmwater) (A&Ww), Full Body Contact (FBC), Fish Consumption (FC), Agricultural Irrigation (AgI), and Agricultural Livestock Watering (AgL).

Arivaca Lake was added to Arizona's CWA Section 303(d) list in 1996 following detection of elevated levels of mercury in fish tissue in samples collected by the Arizona Department of Environmental Quality (ADEQ) and Arizona Game and Fish Department (AZGF). Arizona's 1998 303(d) list shows Arivaca Lake as not supporting uses due to the presence of a Fish Consumption Advisory for mercury. The criterion or guideline used by Arizona to establish Fish Consumption Advisories is an average concentration in target sport fish of greater than 1 mg/kg (ppm) total mercury. Relevant water quality standards and fish tissue criteria are discussed in more detail in Section 3 of this report.

Water and fish tissue quality in Arivaca lake have been sampled by both AZGF and U.S. EPA. To date, mercury concentrations in the water column have not been detected in excess of ambient water quality standards for mercury. In fish tissue, sample average mercury concentrations in excess of the Fish Consumption Guideline have been reported for largemouth bass. In the following paragraphs, sampling of Arivaca Lake is presented in two parts: historical sampling conducted for assessment purposes and EPA Region 9 sampling conducted in 1997-1998 expressly to support TMDL development.

Historical Sampling

Fish Samples. Five largemouth bass were collected from Arivaca Lake by AZGF in 1995. Samples were analyzed for metals concentrations both at AZGF's laboratory and at the EPA Superfund Contract Laboratory Program (CLP) lab in Region 9. Whole body concentrations of 1.28 to 1.81 mg/kg were measured. These concentrations are in excess of the criterion Arizona uses to establish a Fish Consumption Advisory. (The state's criterion is based on measurement of mercury in fish filets; however; mercury tends to collect in the muscle tissue of fish, so filet concentrations are higher than whole body concentrations.) The lake was subsequently listed as impaired in Arizona's Clean Water Act Section 305(b) assessment.

AZGF again sampled fish at Arivaca Lake in May of 1997. Samples were analyzed at the AZGF laboratory. The AZGF methodology uses fish filets, has a detection limit of 0.3 mg/kg wet weight, and is not certified by Arizona, though AZGF results have been consistent with results from certified labs. Eight largemouth bass filets ranged from 0.29 to 1.60 mg/kg mercury wet weight. Filets of two bluegill sunfish were also sampled for mercury. Results are shown in Table 1.

Water Column Sampling. No historical water column sampling (prior to the recent EPA sampling effort described below) has been identified for Arivaca Lake.

Sediment Sampling. Two sediment samples were collected by AZGF in May 1996 from two arms of the lake. The samples were taken by walking out onto the dry bed during a drought period. The samples were analyzed for mercury at the AZGF laboratory and were reported as nondetects at a detection limit of 0.3 mg/kg.

1997-1998 EPA Sampling

Fish Samples. In October 1997, EPA collected 15 largemouth bass from Arivaca Lake for mercury analysis. Nine of the fish were grouped into three 3-fish composites, while the other six were analyzed individually. All fish were analyzed as filets with no skin. The EPA contractor, Frontier Geosciences, conducted the analyses. Results area shown in Table 2.

Water Column Sampling. In October 1997 and July 1998, EPA staff conducted water column depth profiles of Arivaca Lake at 50 meters and 20 meters from the dam, respectively. Field parameters (pH, dissolved oxygen, temperature, and conductivity) were measured at approximately 1-meter intervals, as shown in Figure 3. In 1997, four surface water samples were taken from three locations in Arivaca Lake for laboratory analysis (Figure 4 and Table 3). In 1998, samples were taken for laboratory analysis at three depths to represent the epilimnion, the oxic/anoxic boundary, and the hypolimnion. Results of the analyses of these samples are shown in Table 4.

Lake Sediment Sampling. EPA staff collected lake sediment samples from Arivaca Lake in October 1997 and July 1998. Results of laboratory analysis of these samples are shown in Table 5. Mercury concentrations in the sediment samples are shown graphically in Figure 5.

Table 1. Mercury Concentrations in Fish from Arivaca Lake, May 1997

Sample ID	Species	Total Hg (mg/kg) wet wt	Length (mm)	Whole Body Weight (grams)
AVLMB1	Largemouth bass	1.61	562	2,264
AVLMB2	Largemouth bass	1.4	375	750
AVLMB3	Largemouth bass	1.44	383	755
AVLMB4	Largemouth bass	1.04	386	868
AVLMB5	Largemouth bass	1.08	366	722
AVLMB6	Largemouth bass	0.76	349	644
AVLMB7	Largemouth bass	0.29	307	548
AVLMB8	Largemouth bass	0.62	303	399
AVBGS1	Bluegill sunfish	< 0.20	190	190
AVBGS2	Bluegill sunfish	0.23	280	594

Note: All samples are filets, with no skin.

Table 2. Mercury Concentrations in Fish from Arivaca Lake, October 1997

Sample ID	Species	Total Hg (mg/kg) wet wt	MeHg (mg/kg) wet wt	Length (mm)	Whole Body Weight (grams)
EPA1	Largemouth bass	0.809		300	365
EPA2	Largemouth bass	1.02		300	328
EPA3	Largemouth bass	1.369		377	722
EPA4	Largemouth bass	1.108		450	1,244
EPA5	Largemouth bass	1.219		429	1,250
EPA6	Largemouth bass	0.756		494	1,578
EPA7	Largemouth bass (Small 3-fish composite)	0.8	0.773 (97%)	323 (7a) 333 (7b) 331 (7c) 329 (ave)	458 (7a) 452 (7b) 494 (7c) 468 (ave)
EPA8	Largemouth bass (Medium 3-fish composite)	1.016	0.900 (89%)	401 (8a) 430 (8b) 423 (8c) 418 (ave)	1,036 (8a) 1,149 (8b) 1,024 (8c) 1,070 (ave)
EPA9	Largemouth bass (Large 3-fish composite)	1.37	1.301 (95%)	450 (9a) 460 (9b) 443 (9c) 451 (ave)	1,200 (9a) 1,229 (9b) 1,182 (9c) 1,204 (ave)

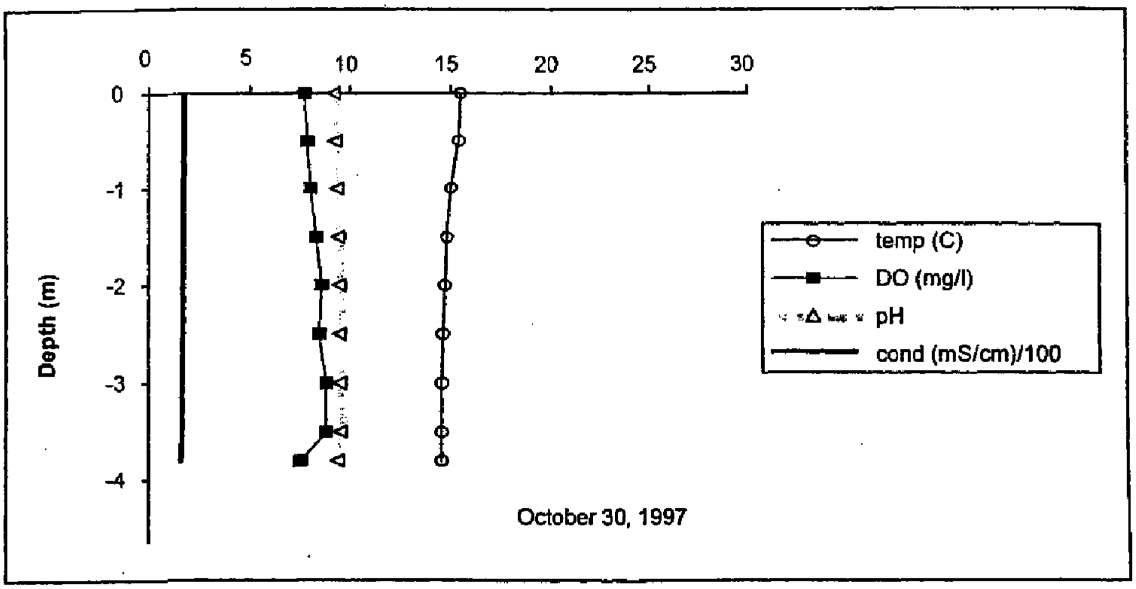
Note: All samples are filets, with no skin. Percentages shown are percent of mercury present as methylmercury.

2.3 Watershed Description

The watershed of Arivaca Lake consists of approximately 12,696 acres. It is almost entirely rural, and is mostly contained within the Coronado National Forest. The watershed was delineated based on examination of topographic maps and the EPA Reach File 3 stream coverage.

The watershed has a semi-arid climate, with abundant rainfall only in July and August. Most of the remainder of the annual precipitation occurs in the winter months. More detail on watershed climate is provided below in the description of the watershed model.

Land use/land cover within the U.S. portion of the watershed was obtained from BASINS Version 2.0 CD (Lahlou et al., 1998), which contains USGS GIRAS land use/land cover data. Coverage for the Arivaca watershed is taken from the Nogales L-157 1:100,000 LU/LC map, compiled in 1973 (USGS, 1990). This identifies land cover using an Anderson Level 2 classification (Anderson et al., 1976). Given the rural nature of the watershed and the lack of newer landuse digital coverages, the 1973 land use/land cover data were judged adequate for watershed modeling. The tabulation of land use/land cover is shown in Table 6 and Figure 6.



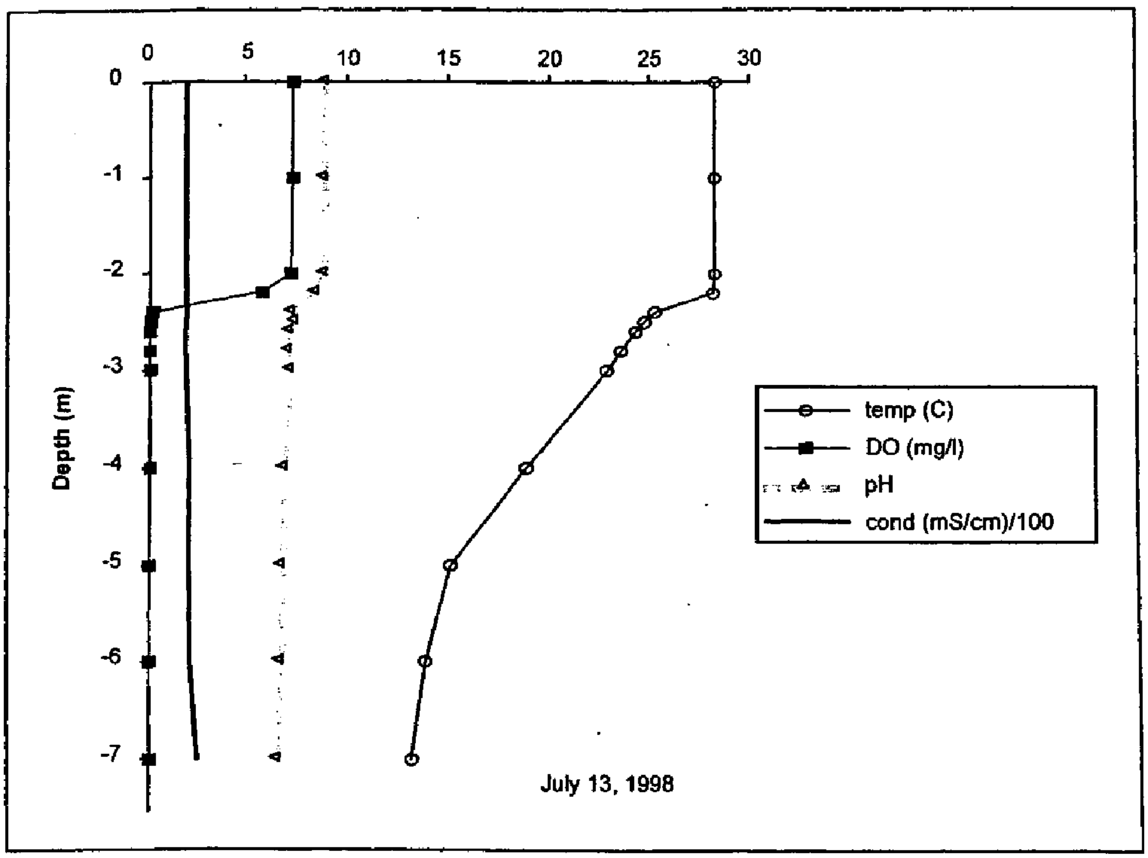


Figure 3. Depth Profiles of Arivaca Lake, October 1997 and July 1998

Table 3. Water quality analyses (surface samples) from Arivaca Lake, October 1997

Sample ID	Sample description	Depth (m)	Total Hg ng/L (ppt)	Diss. Hg ng/L (ppt)	Total MeHg ng/L (ppt)	TSS mg/L	Volatile Solids mg/L	TDS mg/L	DOC mg/L	alk. mg/L	$SO4^{-2}$ mg/L	Ca^{+2} mg/L	Mg^{+2} mg/L	Cl^{-} mg/L
WTR06	150 feet in front of dam near surface total water depth = 3.8 m	near surface	1.46	1.04		10	10	146	18.5	63.9	13.8	18.1	3.8	6.00
WTR02	mouth of Cedar Canyon trib near surface	near surface	1.37	1.07										
WTR03-1	mouth of Cedar Canyon trib near surface	near surface	1.19	1.11										
WTR01	central/long arm, shallow water, near surface	near surface	2.99	1.39										

Note: DOC = dissolved organic carbon, TSS = total suspended solids, alk = total alkalinity, TDS = total dissolved solids.

Table 4. Water quality analyses (depth profile) from Arivaca Lake, July 1998

Sample ID	Sample description	Depth (m)	Total Hg ng/L (ppt)	Diss. Hg ng/L (ppt)	Total MeHg ng/L (ppt)	TSS mg/L	Volatile Solids mg/L	TDS mg/L	DOC mg/L	alk. mg/L	$SO4^{-2}$ mg/L	Ca^{+2} mg/L	Mg^{+2} mg/L	Cl^{-} mg/L
W-15	sample depth = 1.0 m (epilimnion), algal bloom present, high turbidity sampling station: 50 ft from dam total water depth = 7.2 m (24 ft)	1	8.06			16	16	173	15.9	55.4	11.3	20	3.4	6.90
Ariv. MeHg	sample depth = 2.8 m (just below oxic/anoxic boundary), same station as W-15	2.8	22.6		14.3									
W-14	sample depth = 5.5 m (hypolimnion), same station as W-15	5.5	37.5			10	10	165	24.3	90.7	0.21	19.2	3.3	6.60

Note: DOC = dissolved organic carbon, TSS = total suspended solids, alk = total alkalinity, TDS = total dissolvedsolids.

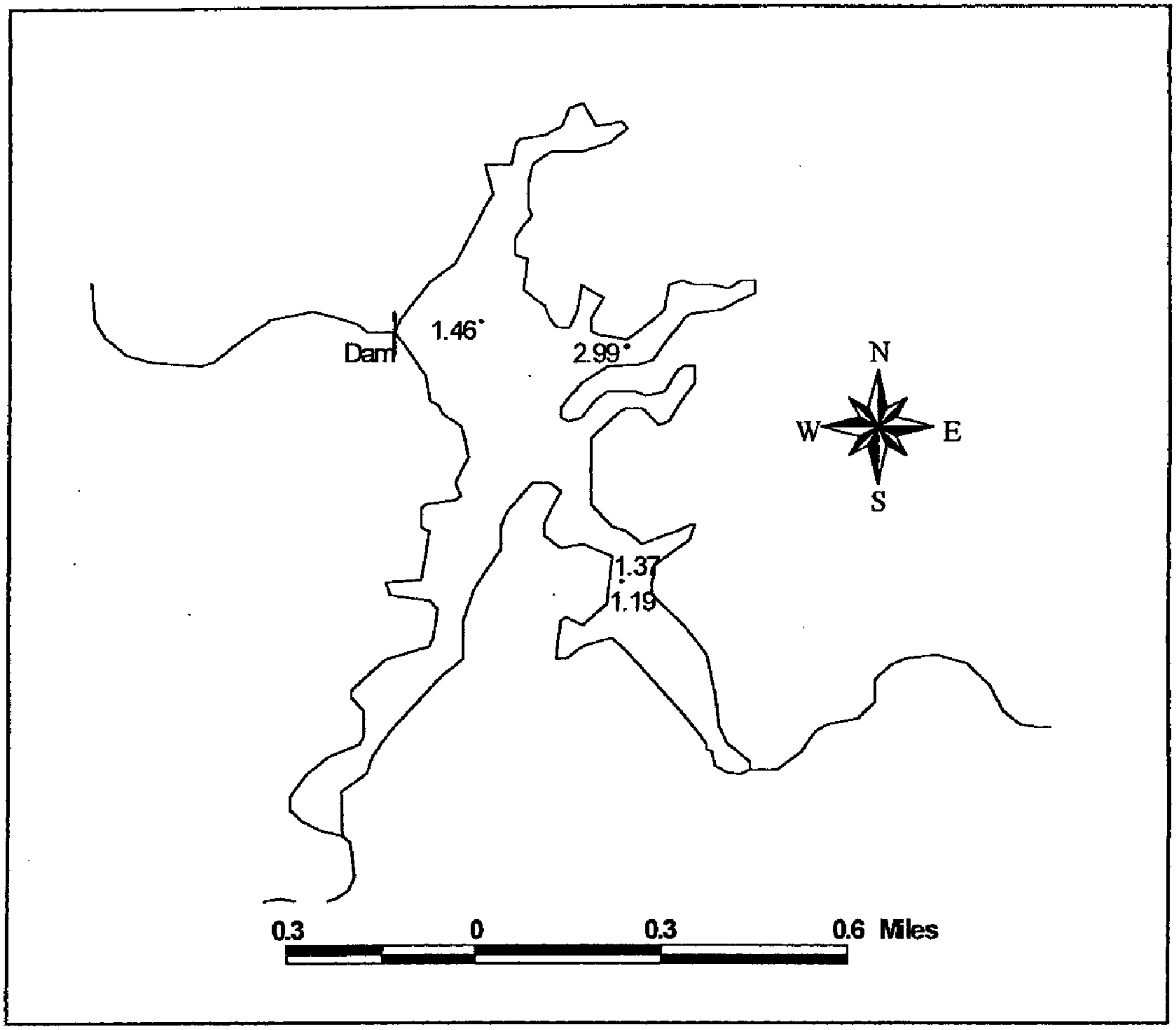


Figure 4. Mercury Concentration (ppt) in Arivaca Lake Surface Water, October 1997.

Table 5. In-Lake Sediment Analyses from Arivaca Lake, October 1997 and July 1998

Sample ID	Site Description	Total Hg (ppb dw)*	MeHg (ppb dw)*	pH	Redox (mV)	Sulfate (ppm)	Sulfide (ppm)	TOC (ppm dw)*	Percent Clay
OCTOBER 1997									
WSHD14-1	wet sediment from arm to north of dam	141						76,700	33.8
WSHD15	lake sediment, water depth of 1 foot: eastern/central arm, across from dam--anaerobic odor	91						45,400	
WSHD16-1	lake sediment, water depth of 1 foot: Cedar Canyon arm--anaerobic odor	87						50,500	
WSHD17	lake sediment, water depth of 1 foot: Chimney Canyon arm--anaerobic odor	113						44,700	22.9
	150 ft in front of dam, water depth of 3.7 m, sample:	192,141				19,774		3,230,028,500	
SDMT02	A: top 2 cm of sediment		0.419	6.86	4				
SDMT01	B: 5 cm of sediment below top 2 cm of sediment		0.290	6.96	-38				
SDMT06	near Cedar Canyon mouth, water depth of 2 m, 1 meter of dense plant life, sample: top 4 cm of sediment	151	0.166	6.7	70	35.4		34,800	
SDMT05	near Chimney Canyon mouth, water depth of 2 m, 1 meter of dense plant life, sample: top 4 cm of sediment	151	0.217	-	-	32.9		30,300	
SDMT03	same as SDMT05 (blind split)	130	0.159	-	-	48.8		27,500	
JULY 1998									
AVM-25	close to boat ramp area water depth =13.5 ft sediment has strong odor Algal bloom present high turbidity	99.8 97.3	0.415	6.3	-61	67	14	30,500	
AVM-26	50 ft from dam water depth = 23 ft sediment has strong odor	117	0.248	6.9	-87	680	190	34,900	
AVM-27	midway between dam and boat ramp water depth = 17 ft	112	0.499	7	-88	32	10	31,900	
AVM-28	same as AVM-26 (blind dup)	147	0.309			520	90		

* dw = dry weight

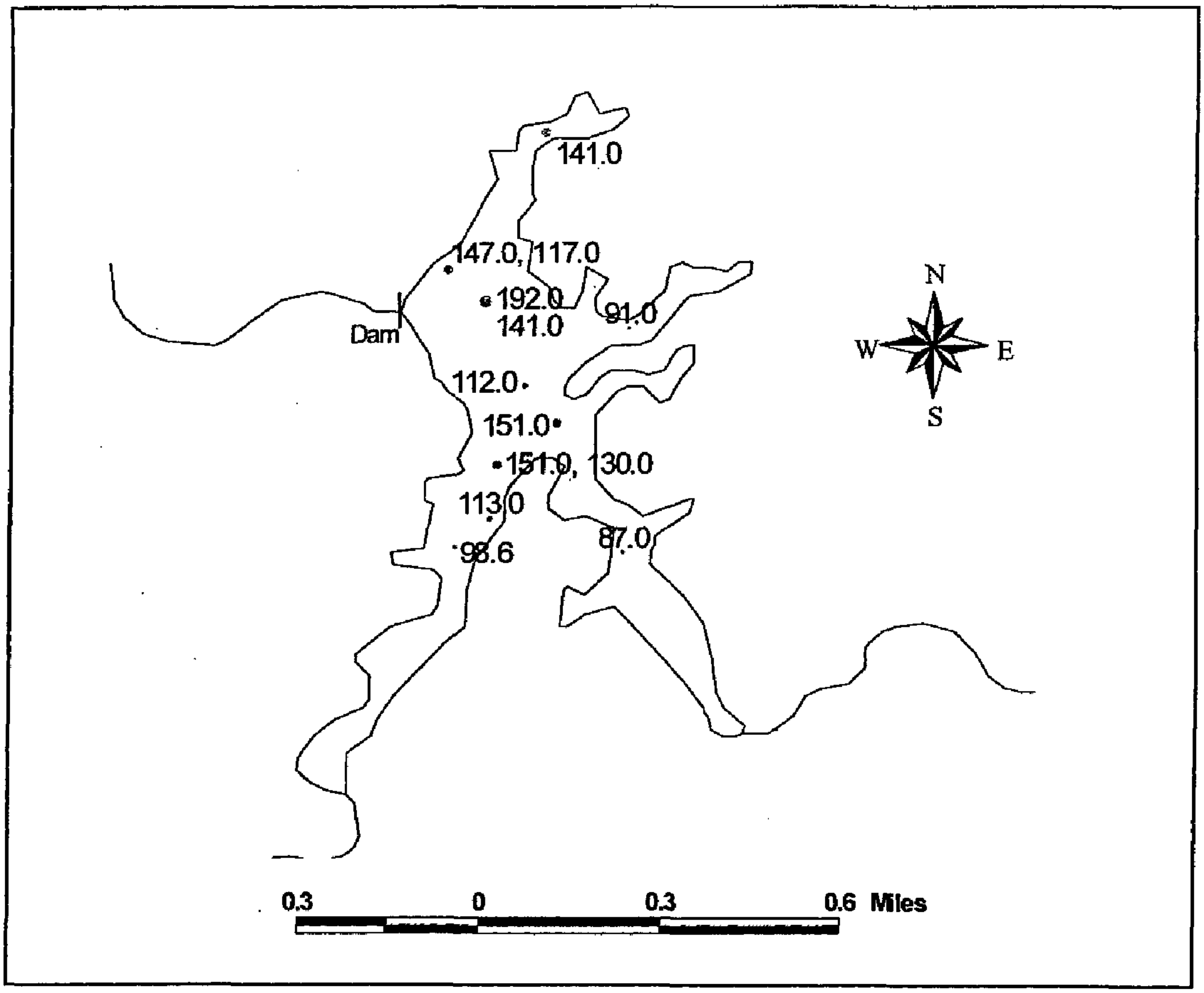


Figure 5. Mercury Concentration (ppb) in Arivaca Lake Sediment, July 1998

Table 6. Land Use/Land Cover for the Arivaca Lake Watershed, 1973

Anderson Level 2 Classification	Acres
Evergreen Forest Land	6,421.1
Reservoirs	67.3*
Shrub and Brush Rangeland	2279
Total	8,767.5

* Less than full pool area, suggesting the lake was below full pool when the coverage was taken.

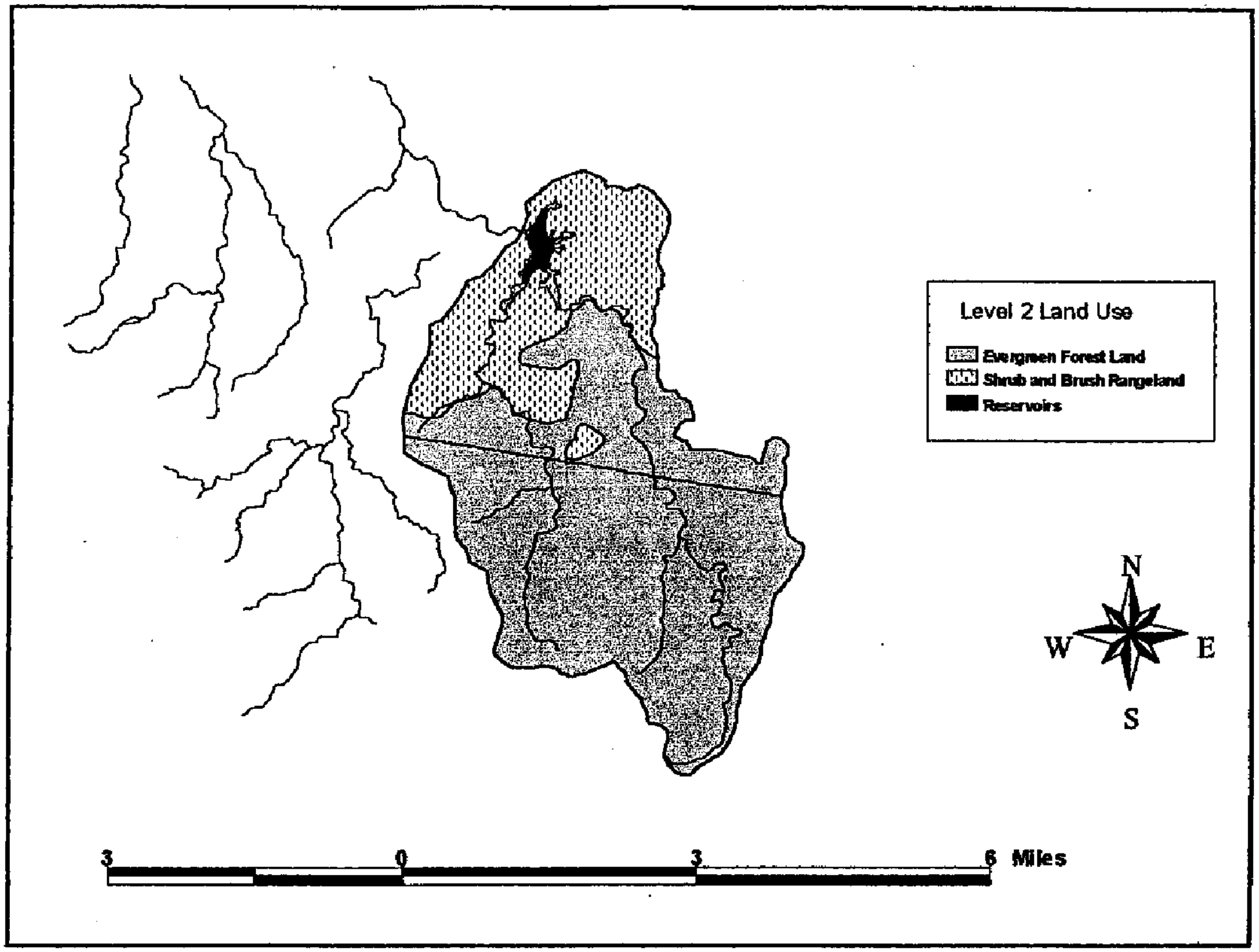


Figure 6. GIRAS Land Use, Arivaca Watershed.

3. Numeric Targets

TMDLs are developed to meet applicable water quality standards. These may include numeric water quality standards, narrative standards for the support of designated uses, and other associated indicators of support of beneficial uses. A numeric target identifies the specific goals or endpoints for the TMDL that equate to attainment of the water quality standard. The numeric target may be equivalent to a numeric water quality standard (where one exists), or it may represent a quantitative interpretation of a narrative standard. This section reviews the applicable water quality standards and identifies an appropriate numeric indicator and associated numeric target level for the calculation of the Arivaca Lake mercury TMDL.

3.1 Numeric Water Quality Standards

Arizona has adopted water quality standards for mercury that apply to a number of the designated uses specified for Arivaca Lake (*Arizona Administrative Code*, R-18-11, Appendix A). The standards for the protection of aquatic life and wildlife are expressed in terms of the dissolved, rather than total recoverable mercury concentration, as recommended by U.S. EPA (FR 60(86): 22229-22237, May 4, 1995). Numeric water quality criteria for mercury applicable to human and agricultural uses are expressed in terms of total recoverable mercury. These water quality standards are summarized in Table 7. None of the mercury criteria are hardness-dependent.

Table 7. Arizona Water Quality Standards for Mercury

Designated Use	Criterion (µg/l)	Chemical Form
Aquatic and Wildlife (Warmwater) (A&Ww)	acute: 2.4 chronic: 0.01	dissolved dissolved
Full Body Contact (FBC)	42.0	total recoverable
Fish Consumption (FC)	0.6	total recoverable
Agricultural Irrigation (AgI)	No numeric criterion	
Agricultural Livestock Watering (AgL)	10.0	total recoverable

The most stringent applicable standard for total recoverable mercury is 0.6 µg/L (FC). The dissolved standards for protection of aquatic life and wildlife include both an acute standard, applicable to short-term exposures, with compliance determined from grab samples, and a chronic standard, applicable to longer-term exposures, with compliance determined from the arithmetic mean of consecutive daily samples collected over a 4-day period (*Arizona Administrative Code*, R-18-11-120.C). To date, mercury concentrations in water in Arivaca Lake (total or dissolved) have not been determined to be in excess of the applicable water quality standards, and Arivaca Lake is listed as not supporting its designated uses based on the presence of a Fish Consumption Advisory, rather than an excursion of ambient water quality standards for mercury.

3.2 Narrative Standards

The state narrative language for toxics is expressed in part as follows (Arizona Administrative Code, R-18-11-108(A)):

> A *surface water shall be free from pollutants in amounts or combinations that:*
>
> *1.* *Settle to form bottom deposits that inhibit or prohibit the habitation, growth, or propagation of aquatic life or that impair recreational uses;*
>
> ...
>
> *5.* *Are toxic to humans, animals, plants, or other organisms;*
>
> ...

These two clauses may be taken to generally prohibit loading of mercury to the lake in amounts that result in fish tissue contamination levels sufficient to impair recreational uses or present a risk to human health.

3.3 Fish Consumption Guidelines

Issuance of a Fish Consumption Advisory for mercury in Arizona is based on 1.0 mg/kg tissue concentration, as recommended by the U.S. Food and Drug Administration (FDA). Fish Consumption Advisories are issued when the average concentration in sport fish is found to exceed this criterion.

U.S. EPA (1995, Table 5-2) recommended a Screening Value for Fish Consumption Guidelines of 0.6 mg/kg tissue concentration total mercury, based on the following assumptions:

- Reference Dose (RfD) for methylmercury of 3×10^{-4} mg/kg/day for adults, reduced by a factor of 5 to estimate an RfD of 6×10^{-5} mg/kg/day for developmental impacts in fetuses and nursing infants.
- Total mercury concentration can be considered approximately equal to methylmercury concentration in fish.
- Average adult consumption rate of 6.5 g/day.
- Average adult body weight of 70 kg.

Since release of the 0.6 mg/kg screening value, the RfD for methylmercury has been revised in EPA's Integrated Risk Information System (IRIS) to 1×10^{-4} mg/kg/day for both developmental and chronic system effects (U.S. EPA, 1997c). U.S. EPA (1997c) did not recalculate a Screening Value; however, use of the revised RfD in the calculations used for the Screening Value in EPA's 1995 guidance would result in a screening value of approximately 1 mg/kg in fish tissue.

Tables 4-8 through 4-10 in U.S. EPA (1997) use the revised RfD to provide recommended monthly consumption limits for chronic systemic health endpoints for the general population, for developmental health endpoints for women of reproductive age, and for developmental health endpoints for children, as a function of methylmercury concentration in fish tissue and average meal size. Calculation of a site-specific standard for Arivaca Lake would require an analysis of the exposed population, including meal size and frequency of consumption. Although the majority of sport fishermen are likely to consume fish from the lake only occasionally, consumption rates might be higher for some local residents.

Although data are not available at this time to compute site-specific, risk-based standards for the protection of human health, the 0.6 and 1.0 mg/kg tissue concentrations lead to the risk-based consumption limits shown in Table 8 (U.S. EPA, 1997c).

Table 8. Recommended Consumption Limits for Methylmercury in Fish (US EPA, 1997c)

	0.6 mg/kg fish tissue	1.0 mg/kg fish tissue
General population, 12-oz meal size	1 meal per month	6 meals per year
Women of reproductive age, 12-oz meal size	1 meal per month	6 meals per year
Children, 4-oz meal size	6 meals per year	NONE

3.4 Wildlife Protection Considerations in Numeric Target Selection

In addition to posing a human health risk through consumption of contaminated fish, mercury can also cause wildlife health effects to predators which are high in the food chain as result of eating mercury contaminated fish. Mercury is believed to bioaccumulate to levels of potential concern for wildlife only in larger, older fish (e.g. largemouth bass who are several years old). The only fish eating birds present in Arizona which are believed to be capable of catching such large fish are bald eagles (personal communication with Sam Rector, ADEQ, August 25, 1999). ADEQ and Arizona Department of Game and Fish report that bald eagles are not regularly found in the Arivaca Lake watershed; nor are nesting bald eagles found nearby (personal communication with Sam Rector, ADEQ, August 25, 1999). Therefore, ADEQ and EPA conclude that potential risk to wildlife from eating mercury contaminated fish from Arivaca Lake is minimal and need not be further addressed in the TMDL.

3.5 Selected Numeric Target for Completing the TMDL

The applicable numeric targets for the Arivaca TMDL are the Arizona water quality standard of 0.2 μg/l total mercury in the water column and the Fish Consumption Guideline criterion of 1 mg/kg total mercury concentration in fish tissue. Water column mercury concentrations have not been found in excess of the ambient water quality standard; however, fish tissue concentrations have consistently exceeded the guideline value. Fish in Arivaca Lake accumulate unacceptable tissue concentrations of mercury even though the ambient water quality standard appears to be met. The most binding regulatory criterion is the fish tissue concentration criterion of 1 mg/kg total mercury, which is selected as the primary numeric target for calculating the TMDL.

Mercury bioaccumulates in the food chain. Within a lake fish community, top predators usually have higher mercury concentrations than forage fish, and tissue concentrations generally increase with age class. Top predators (such as largemouth bass) are often target species for sport fishermen. Arizona's Fish Consumption Guideline is based on average concentrations in a sample of sport fish. Therefore, the criterion should not be applied to the extreme case of the most-contaminated age class of fish within a target species; instead, the criterion is most applicable to an average-age top predator. Within Arivaca Lake, the top predator sport fish is the largemouth bass. The lake water quality model (Section 5.7) is capable of predicting mercury concentrations in fish tissue for each age class at each trophic level. Average mercury concentrations in fish tissue of target species are assumed to be approximated by average concentration in 5-year-old largemouth bass. In the May 1995 sampling of Peña Blanca Lake (see Peña Blanca TMDL report), the average mercury tissue concentration in largemouth bass (1.31 mg/kg) was slightly lower than the average concentration in 5-year-old largemouth bass (1.35 mg/kg), and the average concentrations in all other sampled species were lower than that in largemouth bass. Therefore, the selected target for the TMDL analysis is an average tissue concentration in 5-year-old largemouth bass of 1.0 mg/kg or less.

4. Source Assessment

There are no permitted point source discharges and no known sources of mercury-containing effluent in the Arivaca watershed. External sources of mercury load to the lake include natural background load from the watershed, possible nonpoint loading from past mining activities, and atmospheric deposition.

4.1 Watershed Background Load

The watershed background load of mercury derives from mercury in the parent rock and from the net effects of atmospheric deposition of mercury on the watershed. Because no significant near-field sources of mercury deposition were identified, mercury from atmospheric deposition onto the watershed is treated as part of a general watershed background load in this analysis.

Atmospheric deposition of mercury occurs throughout the world, and mercury is input to the Arivaca watershed through both wet deposition (precipitation) and dry deposition. As described in Section 4.4, atmospheric deposition is estimated to contribute more than 12 micrograms of mercury per square meter per year ($\mu g/m^2/yr$). This atmospheric loading rate is greater than the total load of mercury from the watershed to the lake estimated in Section 5.5; however, portions of the atmospheric mercury deposition are recycled to the atmosphere or sequestered within the watershed.

Some mercury is also present within the parent rock formations of the Arivaca watershed, although no concentrated ore deposits are known (Keith, 1975). Cinnabar (HgS), the primary naturally occurring ore of mercury, typically consists of 86.2 percent mercury and 13.8 percent sulfide. Cinnabar can occur as impregnations and as vein fillings in near surface environments from solutions associated with volcanic activity and hot springs. Cinnabar can also occur in placer-type concentrations produced from the erosion of mercury-bearing rocks. In the nearby Peña Blanca watershed, cinnabar has been reported to occur as traces in irregular and lensing fissure veins in association with argentiferous galena, pyrite, marcasite, and chalcopyrite. Cinnabar is not reported to occur in the mines characterized in the index of mining properties for the Oro Blanca mining district, located just to the south of the Arivaca watershed, which is the only mining district located in or near the Arivaca watershed (Keith, 1975). However, similarities in the geology between the Peña Blanca and Arivaca watersheds would suggest that cinnabar could also be present in the Arivaca watershed.

EPA Watershed Sediment Sampling, 1997

The net contributions of both atmospheric deposition and weathering of native rock were assessed by measuring concentrations in sediment of tributaries to Arivaca Lake. EPA collected 25 sediment and rock samples (including two blind duplicates) from dry tributaries in the Arivaca watershed in October 1997 and analyzed them for total mercury. Mercury concentrations (in parts-per-billion dry weight) are shown in Table 9 and Figure 7. Sediment mercury concentrations were below 150 ppb except for samples at and just downstream of the Ruby Dump site, in the southern end of the watershed. Samples within Ruby Dump had mercury

Table 9. Sediment Analyses from Arivaca Watershed, October 1997

Sample ID	Site Description	Total Hg ppb, dw	TOC ppm, dw	Percent Clay
WSHD07	Chimney Canyon wash, halfway from trail head to Papago Tanks	42	16,000	31.8
WSHD08	rock sample: same location as WSHD07	17 (53*)		
WSHD09	Papago Tanks: southern tank, nearly dry, sample from wet region in center of tank	95	46,200	33
WSHD10	Papago Tanks: northern tank, several feet of water, sample taken below water line	52	25,800	
WSHD11	approx. 1/2 mile downstream of Papago Tanks	61	91,000	
WSHD20	approx. 1 mile downstream of Papago Tanks	107	43,900	31
WSHD21	rock sample: same location as WSHD20	141		
WSHD22	2 miles downstream of Papago Tanks	85	32,200	
WSHD01	Ruby Dump: top of hill, beneath fire pit	1,467	46,600	8.8/12.1
WSHD02	Ruby Dump: middle of hill	495 (1,222*)	24,900	
WSHD03	Ruby Dump: bottom of hill	486	20,400	7.6
WSHD04	blind duplicate (same as WSHD02)	1,244		
WSHD32	approx. 250 feet downstream of Ruby Dump	845	106,000	10.1
WSHD24-2	blind duplicate, same as WSHD32	811	115,000	
WSHD26	approx. 1 mile downstream of Ruby Dump	104	49,200	4
WSHD06a	Boulder Tank, just below water line	125	34,400	27.4
WSHD06b	lab QC (same as WSHD06a)	117		
WSHD05	Bolsa Tank, just below water line	73	31,400	
WSHD36	upper wash feeding Cedar Canyon--SE corner of watershed--upstream of WSHD35, sandy	25	5,790	
WSHD35	upper wash feeding Cedar Canyon--SE corner of watershed, sandy	28	17,200	4.8
WSHD29	Cedar Canyon wash (dry)	75	10,800	
WSHD28	Cedar Canyon wash (dry), silty/sandy	68	98,800	6.6
WSHD27	Cedar Canyon wash (dry)	67	50,700	
WSHD25	Cedar Canyon wash (dry), sandy	25	5,140	3.8
WSHD24-1	from wash feeding Cedar Canyon arm of lake	59	11,100	
WSHD23	near Cedar Canyon arm of lake	31	27,100	

*Reanalysis by Frontier Geosciences

Note: dw = dry weight, TOC = total organic carbon

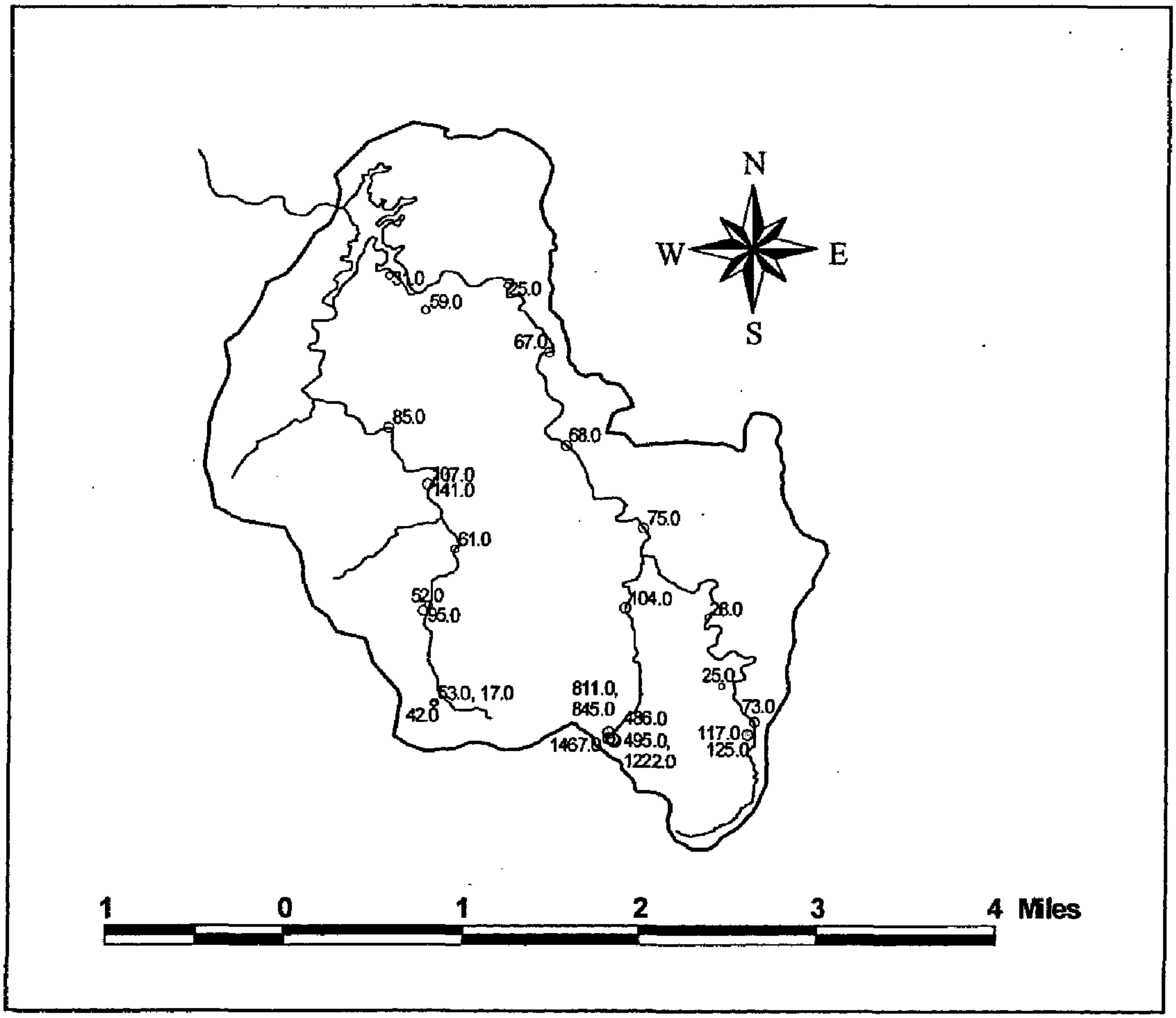


Figure 7. Total Mercury Concentrations (ppb) in Arivaca Lake Tributary Sediment Samples

levels as high as 1467 ppb. Mercury loading from Ruby Dump is discussed further in Section 4.3.

In October 1997, EPA also collected three background sediment samples from just outside the Arivaca Lake watershed, in areas expected to be relatively uncontaminated by anthropogenic sources of mercury. These samples had mercury concentrations of 197, 54 and 12 ppb dry weight. Adriano (1986) found that the normal mercury concentration in soils ranged from 30 to 200 ppb dry weight. Based on these data, most of the sediment samples from the Arivaca watershed may be considered at or near background mercury levels.

4.2 Nonpoint Load from Past Mining Activities

Mercury itself is not known to have been mined in the watershed. Mining activities for minerals other than mercury can nonetheless affect watershed mercury load in two distinct ways. First, mining activity produces tailing residues of crushed rock. If the parent material contains mercury ore, the conversion of rock to tailings increases the amount of mercury ore present in readily erodible form. Second, mercury may be directly used in the gold mining process: before the introduction of cyanidation technology at the beginning of the 20th century, mercury amalgamation of precious metal ores was common practice throughout the western United States. It was common practice to use mercury to amalgamate gold ore in ball mills. In the ball mill process, the raw ore was crushed to a talc consistency and placed into a settling trough with water and elemental mercury. The gold amalgamated with the mercury and settled out. The excess water and overburden were washed out of the trough onto the ground, and the amalgam was collected and placed in a furnace, where the mercury was evaporated off, recondensed into a retort, and saved for reuse. Some loss of mercury occurred in many steps in this metallurgical process. Most of the gold-mercury amalgam settled out and was recovered, but some was inevitably washed out of the trough with the fine overburden. The amalgam furnaces might also have elevated local soil concentrations through short-range atmospheric deposition. Ball mill process mercury is likely to be of greater concern for environmental impact because the residue is more likely to contain soluble species of mercury than low-solubility cinnabar outcrops. Studies of the highly contaminated Carson River area in Nevada (Lechler, 1998) demonstrate that the dominant form of mercury present in amalgamation-process tailings is still elemental mercury, approximately a century after peak mining activity, whereas stream sediments in the tailings area were dominated by elemental and exchangeable forms of mercury. Significant conversion to relatively insoluble cinnabar occurs only when these materials are transported to more anoxic, reducing environments with concentrations of labile sulfur in excess of 0.1 percent by weight. Thus, the mercury contained in ball mill tailings is likely to be more mobile and more bioavailable than the mercury contained in cinnabar in the watershed soils background and tailings residue from hard rock mines which has not been processed by mercury amalgamation.

The mining of precious metals such as gold and silver was common in the area surrounding Arivaca Lake, but apparently not within the watershed itself. The U.S. Bureau of Mines Mineral Availability System/Mineral Industry Location System (MILS) CD-ROM (last updated in 1995) identifies only one exploratory prospect, for manganese and uranium, within the Arivaca watershed.

The mining districts in this area have been documented (Keith, 1975), and the primary drainages have all been surveyed by EPA during sample collection. Although the possibility cannot be ruled out, the likelihood of finding previously unknown additional mill sites or tailings piles in the Arivaca drainage is low. Reconnaissance efforts by AZGF and EPA have not located any obvious ball mill sites within the watershed. AZGF has, however, identified two old mining operations:

- AZGF collected soil samples from the tailings of a mine shaft located just inside the southern boundary of the watershed to the north and west of the town of Ruby. There is a road leading to the mine shaft that intersects Ruby Road just to the west of Ruby. No mercury was detected in samples taken at this location (Will Haze, Fisheries Program Manager, AZGF, personal communication).

- There is a small mine shaft located along Cedar Creek that does not show up on the USGS 1:24,000 topographic map of Arivaca Quadrangle. Soil samples collected in the vicinity of the mine shaft had no detectable mercury (Will Haze, AZGF, personal communication).

4.3 Mercury Loading from Ruby Dump

Ruby Dump is located in the southern portion of Arivaca watershed, at the very upstream end of Cedar Canyon Wash (Figure 8). The dump apparently served the town of Ruby and the Montana Mine. This former mining town is located about 1 mile southwest of the dump site, outside the Arivaca watershed.

The trash in Ruby Dump covers an area of approximately 200 feet by 50 feet. The waste is characterized by numerous mining artifacts (crucibles, etc.), but also includes many common household items such as bottles and plates. The presence of a fire pit at the top of the hill indicates that waste was probably burned for volume reduction/purification purposes. Judging by the remaining inorganics, soft drink bottles and other wastes, the majority of the trash appeared to be about 50 to 100 years old.

Samples were taken at three different locations of the Ruby Dump: top of the hill (just below the fire pit), the middle of the hill, and the base of the dump. The total mercury results for these samples, from the top of the hill to the bottom, were 1467 ppb, 1244 ppb (blind duplicate was 495 ppb), and 486 ppb. The average of these four samples is 918 ppb, which is the number used in the watershed modeling to represent mercury concentration in sediment eroding from this site. The watershed modeling is discussed in the Linkage Analysis (Section 5).

4.4 Atmospheric Deposition

Near-Field Atmospheric Deposition

Significant atmospheric point sources of mercury often cause locally elevated areas of near-field atmospheric deposition downwind. Mercury emitted from man-made sources usually contains both gaseous elemental mercury (Hg(0)) and divalent mercury (Hg(II)). Hg(II) forms, because of their solubility and their tendency to attach to particles, are redeposited relatively close to their source (probably within a few hundred miles) whereas Hg(0) remains in the atmosphere much longer, contributing to long-range transport.

The fact that there is relatively low precipitation in Arizona means that less mercury is likely to be deposited near the source; i.e., Hg(II) forms of mercury probably have time to migrate farther from their source before being scavenged by precipitation or dry depositing as particle-attached mercury. This diminishes the impact of near-field sources relative to the regional background. It is still possible, however, that individual atmospheric point sources might contribute to elevated mercury levels in nearby waterbodies.

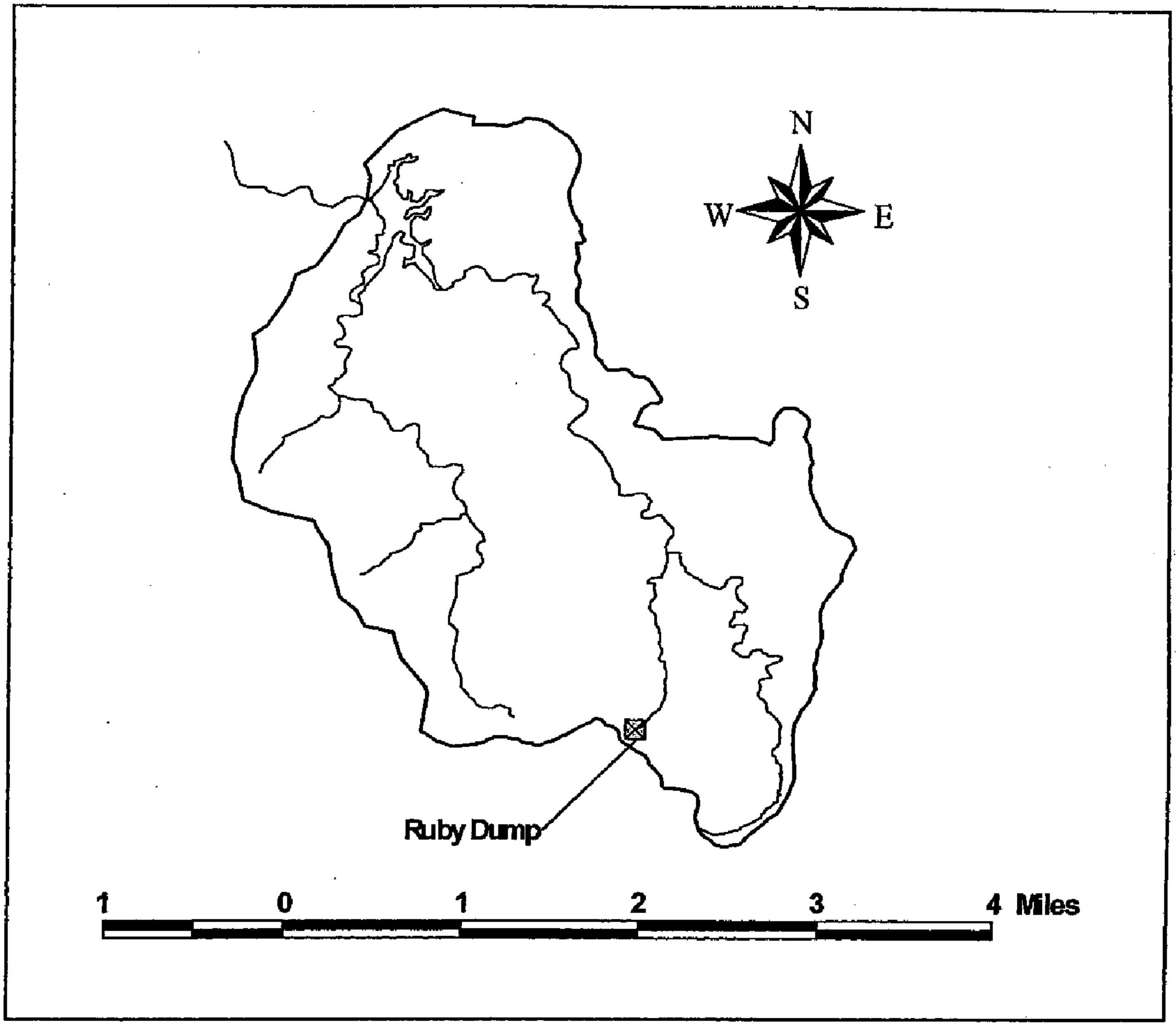


Figure 8. Location Map for Ruby Dump, Arivaca Lake Watershed

Significant potential point sources of airborne mercury include coal-fired power plants, waste incinerators, cement and lime kilns, smelters, pulp and paper mills, and chlor-alkali factories. Based on a review of *Mercury Study Report to Congress* (USEPA, 1997a) and a search of the EPA AIRS database of permitted point sources, there are no significant U.S. sources of airborne mercury within or near the Arivaca watershed.

The prevailing wind direction in the Arivaca watershed is from the southwest, the direction of the Gulf of California. Most nearby parts of Mexico immediately to the southwest of the watershed are sparsely populated. Information provided by Gerardo Monroy and Edna Mendoza of ADEQ (personal communication to Peter Kozelka, U.S. EPA Region 9, April 27, 1999) summarizes what is known of potential Mexican and border mercury emissions:

- The city of Nogales, Sonora is a few miles southeast of the lake at the U.S. border. A study entitled *Air Emission Rate Summary for Stationary Sources in Nogales, Sonora*, compiled by Powers Engineering in 1996, estimated the total mercury emission rate for all stationary mercury sources in Nogales, Sonora, as less than 4 pounds per year. During the Ambos Nogales air quality study some of the teflon filters used in collecting particulate matter samples were analyzed for mercury, and mercury emissions "were not considered significant".
- The nearest lime kiln plants are in Paul Spur, Arizona, just west of Douglas, and south of Aqua Prieta, Sonora, across the border from Douglas. These are all to the east of the watershed and not in the direction of the prevailing wind.
- The Nacozari smelter in Sonora is approximately 150 miles distant from the watershed, to the southeast. A smelter was located at Cananea, Sonora, about 50 miles away (again to the southeast) and is now shut down. There was also a smelter at Douglas, AZ, which shut down around 1986-87.
- The nearest coal-fired electric utility is in the Sulphur Springs Valley, north of Douglas, AZ, approximately 80 miles east of the watershed.

Based on the lack of major nearby sources, particularly sources along the axis of the prevailing wind, near-field atmospheric deposition of mercury attributable to individual emitters is not believed to be a major component of mercury loading to the Arivaca watershed.

Long-Range Atmospheric Deposition

Atmospheric deposition is a major source of mercury in many parts of the country. In a study of trace metal contamination of reservoirs in New Mexico, it was found that perhaps 80 percent of mercury found in surface waters was coming from atmospheric deposition (Popp et al., 1996; Steve Hansen, personal communication, June 13, 1997). In other remote areas (e.g., in Wisconsin, Sweden, and Canada), atmospheric deposition has been identified as the primary (or possibly only) contributor of mercury to waterbodies (Watras et al., 1994; Burke et al., 1995; Keeler et al., 1994).

Wet deposition of mercury has been measured by the Mercury Deposition Network (MDN): in its first year of operation (February 1995-February 1996), the MDN found a volume-weighted average concentration of 10.25 ng/L total mercury in precipitation at 17 stations located mainly in the upper Midwest, Northeast, and Atlantic seaboard (http://nadp.nrel.colostate.edu/NADP/mdn/mdn.html). Volume-weighted average concentration of mercury did vary by station, ranging from 3.62 ng/L at Acadia National Park, Maine, to 13.56 ng/L at Bondville, Illinois. Average weekly wet deposition at the 17 stations ranged from 63 ng/m^2 to 280 ng/m^2.

Only limited monitoring of atmospheric deposition of mercury is available in the Southwest and none from Arizona. Dry and wet deposition were measured in the Pecos River basin of eastern New Mexico in 1993-1994 (Popp et al., 1996). Average weekly deposition rates were calculated to be 140 ng/m^2-wk of mercury from dry deposition and 160 ng/m^2-wk of mercury from wet deposition. These data demonstrate the importance of both dry and wet deposition as sources of mercury.

In May 1997, the MDN began collecting deposition data at a new station in Caballo, in the southwestern quadrant of New Mexico. This station is still approximately 200 miles east of the Arivaca watershed, but it is about 150 miles closer to the subject lake than the Pecos River basin. Original data files for the Caballo station for May 1997 through December 1998 were obtained from the MDN Coordinator. These show an average wet deposition rate of 99 ng/m^2-wk over the period of record, but this estimate is skewed upward by omission of the relatively low-deposition January to April period in 1997. For the complete year of 1998, the deposition rate was 78 ng/m^2-wk. Both estimates are at the lower end of the range seen for other MDN stations due to low precipitation.

It appears that the Caballo MDN station provides the most relevant estimate of mercury deposition at Arivaca Lake. Lack of geographically closer monitoring introduces considerable uncertainty; however, as shown below, direct atmospheric deposition appears to account for only a small portion of the total mercury load to the lake. Even if the direct atmospheric loading rate is underestimated by a significant amount, it would have only a minor effect on the predicted lake response. The Caballo data were therefore selected to characterize mercury wet deposition to the lake surface. The short period of record available was extrapolated to provide estimates across the period of simulation. Two approaches were considered to make this extrapolation: development of a relationship between mercury concentration and rainfall volume, and calculation of average deposition rates. The first approach is based on the observation that mercury wet deposition concentrations are typically inversely related to rainfall volume. There is considerable scatter in this relationship in the Caballo data, particularly at low precipitation volumes. Given this scatter and the short period of record available, the concentration approach was rejected. Instead, it was assumed that cumulative deposition mass was a more robust estimator than concentration. To make maximum use of the available data, the series of all possible running 12-month sums were calculated and then averaged, yielding an annual deposition rate of 4.125 μg/m^2-yr (79 ng/m^2-wk). This annual sum was then apportioned to months based on the observed deposition pattern from May 1997 through April 1998. The observed and scaled wet deposition rates are shown in Figure 9.

The Caballo station does not measure dry deposition. Although there are few direct measurements to support well-characterized estimates, dry deposition of mercury often is assumed to be approximately equal to wet deposition (e.g., Lindberg et al., 1991), as is reported in the Pecos River basin. Throughfall studies in a coniferous forest indicate that dry deposition beneath a forest canopy could be on the order of 50 percent of the wet deposition signal (Lindqvist et al., 1991). Estimated global mercury budgets suggest that dry and wet deposition rates for mercury in deserts are roughly equivalent (Lindqvist et al., 1991). Mercury accumulation rates in wetlands (Delfino et al, 1994) and a seepage lake in Florida (Sigler, 1998) indicate that dry deposition rates are highly uncertain, and could range from negligible to three times wet deposition rates. In wet climates, such as Florida, where scavenging of reactive gaseous mercury (RGM) and aerosol mercury is extensive, the ratio of dry to wet deposition is likely smaller than would occur in more arid environments. Given the low annual rainfall at

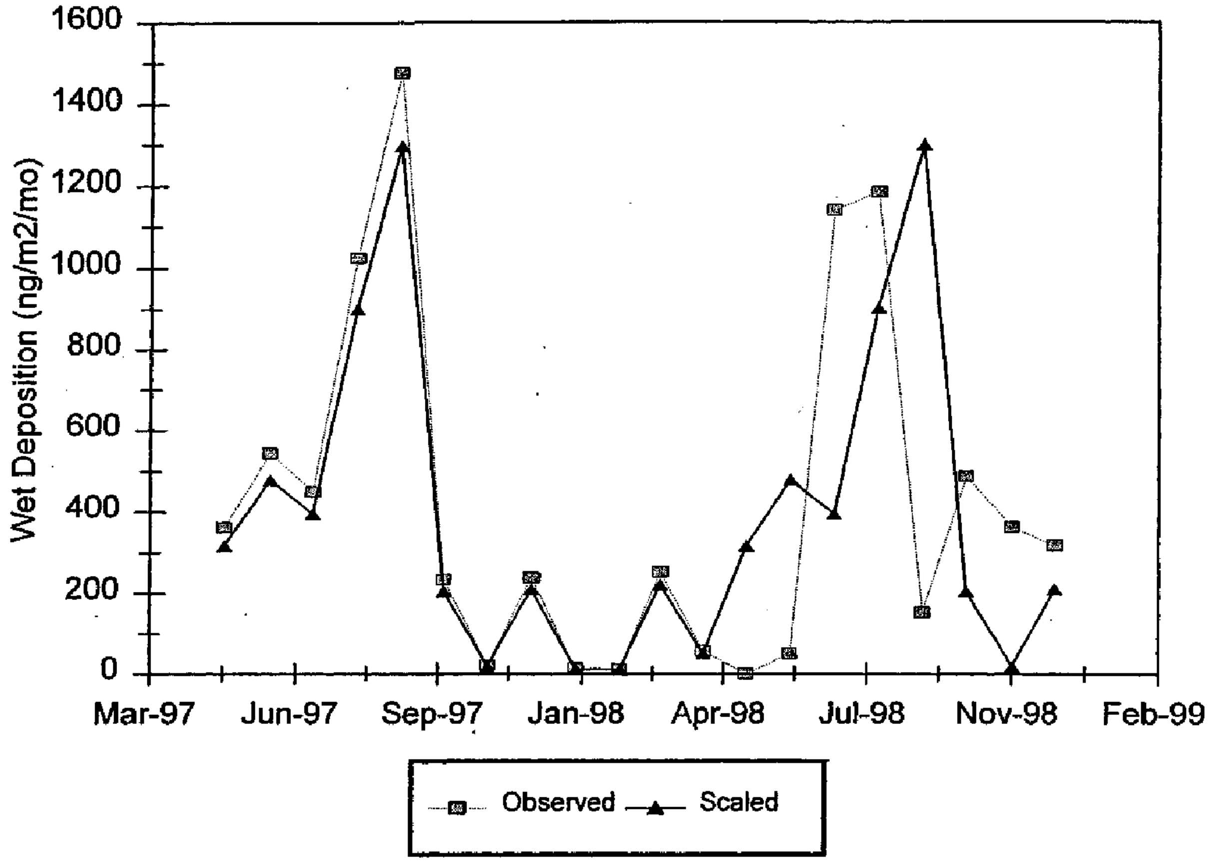


Figure 9. Observed and Scaled Mercury Wet Deposition at Caballo, NM.

Caballo, a ratio of dry to wet deposition greater than 1 is appropriate, and it was conservatively assumed that dry deposition at this station is approximately twice wet deposition. This estimate is consistent with the estimate supplied by the local university cooperator at the Caballo station (Colleen Caldwell, personal communication to Peter Kozelka, U.S. EPA Region 9, cited in Kozelka memo dated April 22, 1999). With this assumption, total atmospheric deposition of mercury (wet and dry) at Caballo was estimated to be 12.4 $\mu g/m^2/yr$, which is close to the total (wet and dry) deposition rate estimated for the Pecos River basin of 15.6 $\mu g/m^2/yr$.

The total mercury deposition rate at Caballo is assumed to apply to Arivaca Lake. Because the climate at Arivaca is wetter than at Caballo, the distribution of wet and dry deposition is likely to be different. Monthly wet deposition rates at Arivaca were estimated as the product of the volume-weighted mean concentration for wet deposition at Caballo times the rainfall depth at Arivaca. This approach was used because volume-weighted mean concentrations are usually much more stable between sites than wet deposition rates, which are sensitive to rainfall amount. Dry deposition at Arivaca was then calculated as the difference between the total deposition rate at Caballo and the estimated Arivaca wet deposition rate. The estimates derived for Arivaca are 5.3 $\mu g/m^2/yr$ by wet deposition and 7.1 $\mu g/m^2/yr$ by dry deposition. In sum, total mercury deposition at Arivaca is assumed to be equivalent to that estimated for Caballo, New Mexico, but

Arivaca is estimated to receive greater wet deposition and less dry deposition than Caballo because more of the particulate mercury and reactive gaseous mercury that contribute to dry deposition will be scavenged at a site with higher rainfall.

In comparison, U.S. EPA's (1997b) national-scale RELMAP modeling estimates total mercury deposition for this part of Arizona to be on the order of 1 to 3 $\mu g/m^2/yr$, which is in the lower end of the simulated range for the continental United States of 0.02 to 80.3 $\mu g/m^2/yr$. The RELMAP modeling is not, however, considered reliable for the border area due to uncertainty as to Mexican emissions.

5. Linkage Analysis

The linkage analysis defines the connection between numeric targets and identified sources. The linkage is defined as the cause-and-effect relationship between the selected indicators, associated numeric targets, and the identified sources. This provides the basis for estimating total assimilative capacity and any needed load reductions. Specifically, models of watershed loading of mercury are combined with a model of mercury cycling and bioaccumulation in the lake. This enables a translation between the numeric target (expressed as a fish tissue concentration of mercury) and mercury loading rates. The loading capacity is then determined via the linkage analysis as the mercury loading rate that is consistent with meeting the target fish tissue concentration.

The linkage analysis is first expressed qualitatively in the form of a risk hypothesis. Based on the conceptual form of the risk hypothesis, quantitative tools are then developed to complete the linkage.

5.1 The Mercury Cycle

Development of the risk hypothesis requires an understanding of how mercury cycles in the environment. Mercury chemistry in the environment is quite complex: mercury has the properties of a metal (including great persistence due to its inability to be broken down), but also has some properties of a hydrophobic organic chemical due to its ability to be methylated via a bacterial process. Methylmercury is easily taken up by organisms, and tends to bioaccumulate; it is very effectively transferred through the food web, magnifying at each trophic level. This can result in high levels of mercury in organisms high on the food chain, despite nearly unmeasurable quantities of mercury in the water column. In fish, mercury is not usually found in levels high enough to cause the fish to exhibit signs of toxicity, but wildlife that habitually eat contaminated fish are at risk of accumulating mercury at toxic levels, and the mercury in sport fish can present a potential health risk to humans.

Selected aspects of the lake and watershed mercury cycle are summarized schematically in Figure 10. The boxes represent stores of mercury, while the arrows represent fluxes. The top of the diagram summarizes the various forms of mercury which may be loaded to a lake. It is important to recognize that mercury exists in a variety of forms, including elemental mercury (Hg(0)), ionic mercury (Hg(I) and Hg(II)), and compounds in which mercury is joined to an organic molecule. In the figure, Hg(I) is ignored, as Hg(II) generally predominates in aquatic systems. Mercuric sulfide (HgS or cinnabar) is a compound formed from Hg(II), but is shown separately, as it is the predominant natural ore. Organic forms of mercury include methylmercury (CH_3Hg or "MeHg"), and also other organic forms, including natural forms such as dimethylmercury and man-made compounds such as organic mercury pesticides. (Where sorption and desorption are indicated in the model diagram, "Hg(II)" and "MeHg" refer to the same common pools of water column Hg(II) and MeHg shown in the compartments at the top of the diagram.)

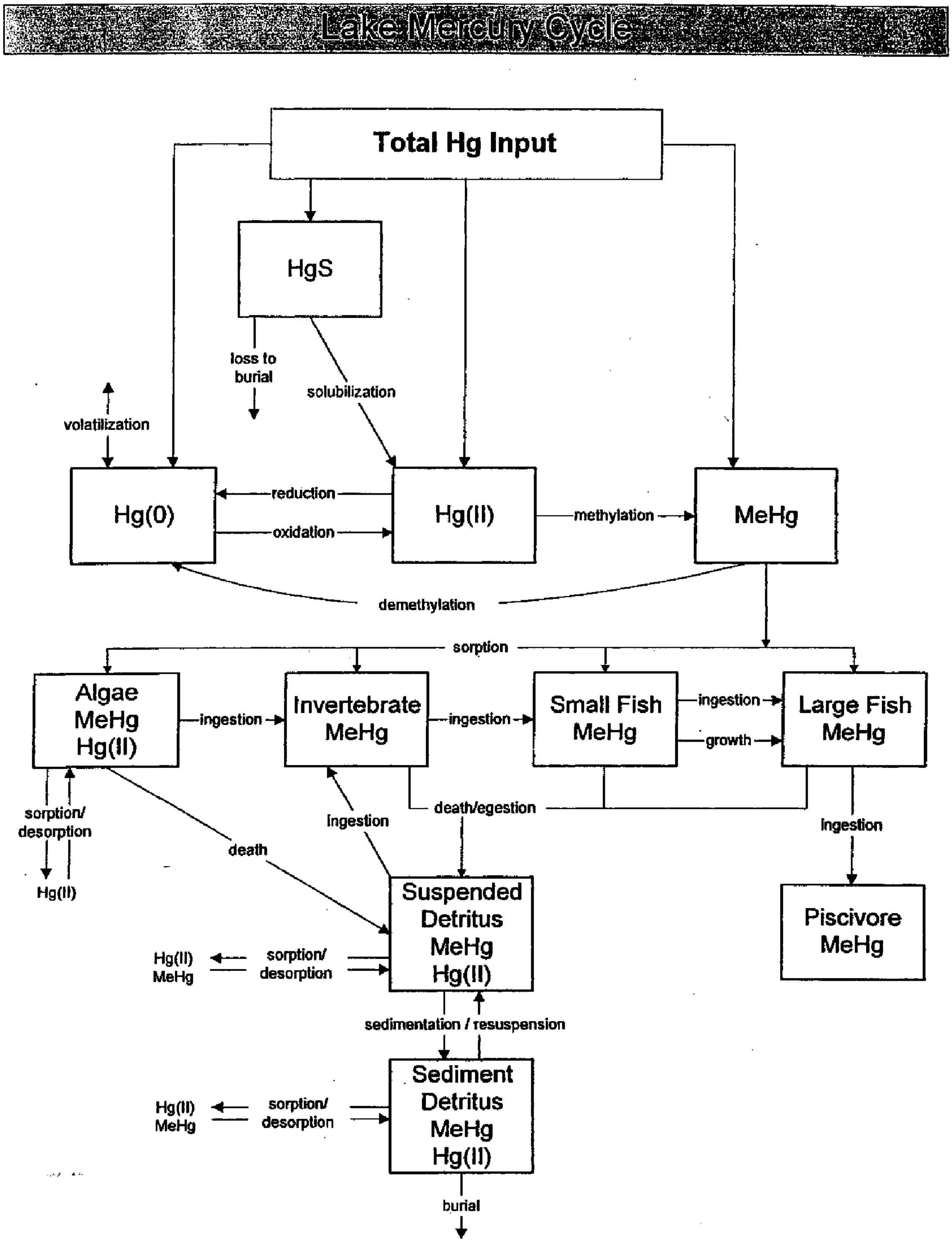


Figure 10. Conceptual Diagram of Lake Mercury Cycle

In the lake mercury cycle, it is critical to consider the distribution of mercury load between the various forms. The major forms reaching a lake from the watershed can have different behavior:

- Mercuric sulfide (HgS), which can be washed into the lake as a result of weathering of natural cinnabar outcroppings. HgS has low solubility under typical environmental conditions and would be expected to be settle out to the bottom sediments of the lake. However, under aerobic conditions, Hg(II) may be liberated by a bacteria-mediated oxidation of the sulfide ion. This Hg(II) would then be much more bioavailable and would be available for methylation. Alternatively, under anaerobic conditions, HgS may be formed from Hg(II).
- Methylmercury (MeHg), which is found in rainfall and may be found in small amounts in mine tailings or wash sediments. It is more soluble than HgS and has a strong affinity for lipids in biotic tissues.
- Elemental mercury (Hg(0)), which may remain in mine tailings, as has been noted in tailings piles from recent gold mining in Brazil. Elemental mercury tends to volatilize into the atmosphere, though some can be oxidized to Hg(II).
- Other mercury compounds that contain and may easily release ionic Hg(II). Such compounds are found in the fine residue left at abandoned mine sites where mercury was used to draw gold or silver out of pulverized rock.

Note that dimethylmercury (CH3-Hg-CH3) is ignored in the conceptual model shown in Figure 10, because this species seems to occur in measurable quantities only in marine waters. Organic mercury pesticides also have been ignored in this TMDL study since such pesticides are not currently used in this country and past use is probably insignificant as there is little cropland in the Arivaca watershed.

Mercury and methylmercury form strong complexes with organic substances (including humic acids) and strongly sorb onto soils and sediments. Once sorbed to organic matter, mercury can be ingested by invertebrates, thus entering the food chain. Some of the sorbed mercury will settle to the lake bottom; if buried deeply enough, mercury in bottom sediments will become unavailable to the lake mercury cycle. Burial in bottom sediments can be an important route of removal of mercury from the aquatic environment.

Methylation and demethylation play an important role in determining how mercury will accumulate through the food web. Hg(II) is methylated by a biological process that appears to involve sulfate-reducing bacteria. Rates of biological methylation of mercury can be affected by a number of factors. Methylation can occur in water, sediment, and soil solution under anaerobic conditions, and to a lesser extent under aerobic conditions. In lakes, methylation occurs mainly at the sediment-water interface and at the oxic-anoxic boundary within the water column. The rate of methylation is affected by the concentration of available Hg(II) (which can be affected by the concentration of certain ions and ligands), the microbial concentration, pH, temperature, redox potential, and the presence of other chemical processes. Methylation rates appear to increase at lower pH. Demethylation of mercury is also mediated by bacteria.

Note that both Hg(II) and methylmercury (MeHg) sorb to algae and detritus, but only the methylmercury is assumed to be passed up to the next trophic level (inorganic mercury is relatively easily egested). Invertebrates eat both algae and detritus, thereby accumulating any MeHg that has sorbed to these. Fish eat the invertebrates and either grow into larger fish (which have been shown to have higher body burdens of mercury) or are eaten by larger fish. At each trophic level, a bioaccumulation factor must be assumed to represent the magnification of mercury concentration that occurs as one steps up the food chain.

Typically, almost all of the mercury found in fish (greater than 95 percent) is in methylmercury form. Studies have shown that fish body burdens of mercury increase with increasing size or age of the fish, with no signs of leveling off.

Although it is important to identify sources of mercury to the lake, there may be fluxes of mercury within the lake that would continue nearly unabated for some time even if all sources of mercury to the lake were eliminated. In other words, compartments within the lake probably currently store a significant amount of mercury, and this mercury can continue to cycle through the system (as shown in the conceptual diagram, Figure 10) even without an ongoing outside source of mercury. The most important store of mercury within the lake is likely to be the bed sediment. Mercury in the bed sediment may be cause exposure to biota by being

- Resuspended into the water column, where it is ingested or it adsorbs to organisms that are later ingested.
- Methylated by bacteria. The methylmercury tends to attach to organic matter, which may be ingested by invertebrates and thereby introduced to the lake food web. It is methylmercury that poses the real threat to biota due its strong tendency to accumulate in biota and magnify up the food chain.

5.2 Cross-Sectional/Reference Site Approach

The complex nature of mercury cycling in the environment can introduce considerable uncertainty into linkage analysis modeling. From examination of a single waterbody, it is difficult to determine the relative contributions of gross mercury loading, internal mercury cycling, and rates of mercury methylation and food chain accumulation to observed body burdens in fish.

Additional constraints on the analysis can be developed by examination of several lakes within the same region simultaneously (cross-sectional approach). Explaining the differences in mercury load, cycling, and bioaccumulation among several lakes provides a robust basis on which to develop the conceptual model. Therefore, the linkage analysis for Arivaca Lake has been developed simultaneously with analyses for Peña Blanca Lake and Patagonia Lake. A mercury TMDL is also required for Peña Blanca Lake, and is being established concurrent with the Arivaca Lake TMDL. Patagonia Lake is also within the same region, yet it has acceptable fish tissue mercury concentrations. Patagonia thus serves as an unimpaired reference site for the cross-sectional analysis. The basic physical characteristics of the three lakes and their watersheds are compared in Table 10.

All three lakes lack known point source discharges of mercury and have a fairly similar distribution of rural rangeland and forest land uses. The Patagonia watershed has far more historical gold mining operations (but also a much larger watershed area), but it is not known how many (if any) of the Patagonia mines are associated with mercury-contaminated ball mill sites. EPA has not detected elevated sediment mercury in the Patagonia watershed. Physically, Patagonia differs from Peña Blanca and Arivaca in having a much larger volume, a larger contributing watershed, and a shorter hydraulic residence time. Patagonia is also the deepest of the three lakes.

EPA collected data from all three lakes and their watersheds in July 1998, which provides a valuable basis for cross-sectional comparison. All three lakes were strongly stratified with anoxic hypolimnia at the time of sampling.

Table 10. Cross-Sectional Comparison of Studied Lakes

	Peña Blanca Lake	Arivaca Lake	Patagonia Lake
Surface area (acres)	49	90	200
Volume at full pool (acre feet)	1071	1050	11000
Average depth (ft)	21.8	11.7	29.1
Maximum depth (ft)	60	25	86
Estimated hydraulic residence time (yrs), 1985-98 average	0.36	0.33	0.16
Watershed area (ac)	8820.6	12696.4	145904
Rangeland (ac)	845.9	5761.3	55509.7
Evergreen Forest (ac)	7906.7	6421.1	88503.8
Cropland and Pasture (ac)	0	420.3	1204.2
Urban and Residential (ac)	33.2	26.5	408.2
Water	34.8	67.3	278.1
Producing mines identified in MILS	4 inactive	none	88 inactive 6 active
Mines producing gold	2 inactive	none	51 inactive 1 active

Notes: "Active" mines include those on temporary shutdown as of the 1995 MIL. Prospects are omitted from the tabulation.

At the time of the July sampling, all three lakes had similar total mercury concentrations in the sediment but very different concentrations in the water column. Lake sediment concentrations in Peña Blanca were somewhat elevated relative to Arivaca and Patagonia. All three lakes showed significant amounts of methylmercury in sediment, but Patagonia, unlike Arivaca and Peña Blanca, did not have much methylmercury in the water column. This seems to explain why fish have unacceptable levels of mercury contamination in Arivaca and Peña Blanca, but not in Patagonia.

The July data emphasize that there may be little correlation between the total mercury mass stored in lake sediments and mercury concentration in fish. Sediment concentrations in Patagonia Lake of both total mercury and methylmercury were higher than those observed in Arivaca, yet Patagonia Lake has acceptable fish tissue concentrations while Arivaca does not. Sediment concentrations of total mercury in Peña Blanca were three times those in Arivaca, but total mercury concentrations in the water column were about twice as high in Arivaca as in Peña Blanca. These observations–indicating that total mercury concentrations in sediment are not linearly related to fish body burden—suggest that the linkage analysis requires a model that can describe the relationship between external mercury load and methylmercury generation.

Why are mercury levels in the water column higher in Arivaca and Peña Blanca than in Patagonia, despite rather similar sediment concentrations? Strong clues emerge from the water column chemistry results from the July sampling. As shown in Table 11, sulfate is strongly elevated in the hypolimnion of Patagonia relative to the other lakes, while alkalinity and pH are also elevated and DOC is somewhat depressed.

These observations suggest that relatively high sulfate concentrations (under alkaline conditions) promote precipitation of cinnabar in Patagonia, thus reducing water column concentrations. Differences in sediment chemistry might also play an important role. The sediment of Patagonia Lake has a stronger reducing environment and lower organic carbon content than the other two lakes. Finally, Patagonia is the deepest lake, which might reduce growth of algae and photosynthetic bacteria at the sediment interface.

Table 11. Comparison of Summer Hypolimnetic Water Chemistry between Studied Lakes

	Patagonia	Arivaca	Peña Blanca
Sulfate (mg/L)	185	0.2	7
Alkalinity (mg/L)	156	91	86
pH	7.5	6.6	7
DOC (mg/L)	7	24	10
Total Hg (ng/L)	2	38	20
MeHg (ng/L)	0.8	14.3	3.9
Total Hg in sediment (ug/kg)	148	129	360
MeHg in sediment (ug/kg)	0.45	0.30	0.95

5.3 Risk Hypotheses

In sum, the key differences between the lakes appear to be in water chemistry and in consequent effects on mercury speciation and cycling, rather than in gross total mercury load (as indicated by sediment concentration). Prior to model development, this understanding was summarized in a risk hypothesis as follows:

- Mercury concentrations in fish are driven by summer methylmercury concentrations in the epilimnion.
- Summer methylmercury concentrations in the epilimnion are driven by mixing from methylmercury concentrations in the hypoxic zone just below the thermocline.
- Methylmercury concentrations below the thermocline are determined primarily by water chemistry and its effect on mercury methylation in the anoxic portion of the water column and/or cycling between the water and sediment, and only secondarily by mercury concentration in the sediment or gross mercury loads.
- Total mercury concentration in the sediments is driven by watershed loads but reflects accumulation over relatively long periods of time and changes only slowly.

The linkage analysis components described in the following sections are designed to provide a quantitative investigation of this risk hypothesis. The linkage tools are separated into several general components. The first two components address the watershed, while the third and fourth address the lake itself. First is a watershed hydrologic and sediment loading model (Section 5.4), which represents the movement of water and sediment from the watershed to the lake. This model supports an analysis of watershed loading of mercury to the reservoir (Section 5.5). A lake hydrologic model is presented in Section 5.6. Finally, a model of lake mercury cycling and bioaccumulation (Section 5.7) is used to address the cycling of mercury in the lake among and between abiotic and biotic components. When combined, these components enable completion of the TMDL linkage analysis.

5.4 Watershed Hydrologic and Sediment Loading Model

An analysis of watershed loading could be conducted at many different levels of complexity, ranging from simple export coefficients to a dynamic model of watershed loads. Data are not, however, available to parameterize or calibrate a detailed representation of flow and sediment delivery within the watersheds. Therefore, a relatively simple, scoping-level analysis of watershed mercury load, based on an annual mass balance of water and sediment loading from the watershed, is used for the TMDL. Uncertainty introduced in the analysis by use of a simplified and uncalibrated watershed loading model must be addressed in the Margin of Safety.

Watershed-scale loading of water and sediment was simulated using the Generalized Watershed Loading Function (GWLF) model (Haith et al., 1992). The complexity of this loading function model falls between that of detailed simulation models, which attempt a mechanistic, time-dependent representation of pollutant load generation and transport, and simple export coefficient models, which do not represent temporal variability. GWLF provides a mechanistic, simplified simulation of precipitation-driven runoff and sediment delivery, yet is intended to be applicable without calibration. Solids load, runoff, and ground water seepage can then be used to estimate particulate and dissolved-phase pollutant delivery to a stream, based on pollutant concentrations in soil, runoff, and ground water.

GWLF simulates runoff and streamflow by a water-balance method, based on measurements of daily precipitation and average temperature. Precipitation is partitioned into direct runoff and infiltration using a form of the Natural Resources Conservation Service's (NRCS) Curve Number method. The Curve Number determines the amount of precipitation that runs off directly, adjusted for antecedent soil moisture based on total precipitation in the preceding 5 days. A separate Curve Number is specified for each land use by hydrologic soil grouping. Infiltrated water is first assigned to unsaturated zone storage, where it may be lost through evapotranspiration. When storage in the unsaturated zone exceeds soil water capacity, the excess percolates to the shallow saturated zone. This zone is treated as a linear reservoir that discharges to the stream or loses moisture to deep seepage, at a rate described by the product of the zone's moisture storage and a constant rate coefficient.

Flow in rural streams may derive from surface runoff during precipitation events or from ground water pathways. The amount of water available to the shallow ground water zone is strongly affected by evapotranspiration, which GWLF estimates from available moisture in the unsaturated zone, potential evapotranspiration, and a cover coefficient. Potential evapotranspiration is estimated from a relationship to mean daily temperature and the number of daylight hours. In the arid Southwest, evapotranspiration often exceeds moisture supply, so stream runoff occurs sporadically in response to precipitation exceeding infiltration capacity. All the streams feeding Arivaca Lake are classified by USGS as intermittent and lack a consistent base flow component.

Monthly sediment delivery from each land use is computed from erosion and the transport capacity of runoff, whereas total erosion is based on the Universal Soil Loss Equation (Wischmeier and Smith., 1978), with a modified rainfall erosivity coefficient that accounts for the precipitation energy available to detach soil particles (Haith and Merrill, 1987). Thus, erosion can occur when there is precipitation, but no surface runoff to the stream; delivery of sediment, however, depends on surface runoff volume. Sediment available for delivery is accumulated over a year, although excess sediment supply is not assumed to carry over from one year to the next.

GWLF Model Input

GWLF application requires information on land use, land cover, soil, and parameters that govern runoff, erosion, and nutrient load generation.

Land Use/Land Cover. The development of the watershed delineation and land use/land cover is described above under Watershed Description (Section 2.3). The watershed delineation was overlain on the STATSGO soil coverage to identify soil groups and associated hydrologic soil groups. Major soil groups for the Arivaca watershed are summarized in Table 12.

Table 12. STATSGO Soil Groups for Arivaca Watershed

Soil ID	Predominant Soil Groups	Soil Hydrologic Group
AZ060	Whitehouse, Berenardino, Hathaway	C
AZ272	Lithic, Rock Outcrop	D
AZ277	Timhus, Quintara, Flugle	B

Rainfall and Runoff Input Data and Parameters

Meteorology: Hydrology in GWLF is simulated by a water-balance calculation, based on daily observations of precipitation and temperature. Precipitation in southern Arizona shows considerable local geographic variability, primarily due to orographic (elevation) effects, with higher precipitation at higher elevations. The nearest first-order weather surface meteorological station is at Tucson International Airport; however, this is well to the northeast and at a lower elevation (2,548 ft MSL) than the Arivaca watershed (lake elevation about 3,800 ft MSL with much of the watershed above 4,000 ft). A search was made of available NOAA Cooperative Summary of the Day (SOD) reporting stations, as well as daily stations reporting to the AZMET network. Based on this review, the most appropriate available meteorological data appear to be those from the SOD station Arivaca 1E (Coop ID 021809) located at the town of Arivaca at elevation 3,619 feet MSL at 31°34' N, 111°20' W. This station supplies only daily precipitation data. Daily maximum and minimum temperatures were taken from Nogales 6N (Coop ID 025924), located at elevation 3,559 feet MSL at 31°27' N, 110°58'W. This station supplies both daily precipitation and maximum/minimum temperatures.

The Arivaca 1E station is at a slightly lower elevation than the Arivaca watershed. To assess the importance of local orographic effects, a double mass analysis was used to compare Arivaca precipitation to records from Canelo 1 NW (Coop ID 021231), located at elevation 5,009 feet MSL, but further from the Arivaca watershed at 31°34' N, 110°32' W. Comparison of the Arivaca and Canelo records did not reveal any consistent trends in precipitation, so Arivaca records were used to represent the entire watershed.

Online data for Arivaca 1E were obtained for January 1985-November 1997 from the Arizona Climate Center (http://climate.usu.edu/free/USA_AZ.HTM), while data for December 1997-December 1998 were purchased from the National Climatic Data Center. No data are missing within the 1985-1998 time period. Precipitation is primarily in the form of rain, with rare snow events.

Average total precipitation and mean daily temperature by month for the 1985-1998 time period are summarized in Table 13. Monthly precipitation is variable from year to year, as shown in Figure 11; however, there are typically two wetter seasons, one in July-August, and one in December-February.

Table 13. Climate Normals for Arivaca (with Temperature from Nogales 6N), 1985-1998.

Month	Average Total Precipitation (inches)	Average Air Temperature (Fahrenheit)	Maximum Air Temperature (Fahrenheit)	Minimum Air Temperature (Fahrenheit)
January	1.36	45.90	83.00	13.00
February	1.82	49.13	85.00	14.00
March	1.26	53.40	93.00	18.00
April	0.37	59.35	99.00	25.00
May	0.31	66.45	103.00	29.00
June	0.17	75.03	112.00	39.00
July	4	79.30	109.00	47.00
August	4.91	78.26	107.00	49.00
September	1.65	72.75	100.00	38.00
October	1.05	63.47	98.00	24.00
November	1.04	52.34	87.00	14.00
December	1.71	45.99	81.00	10.00

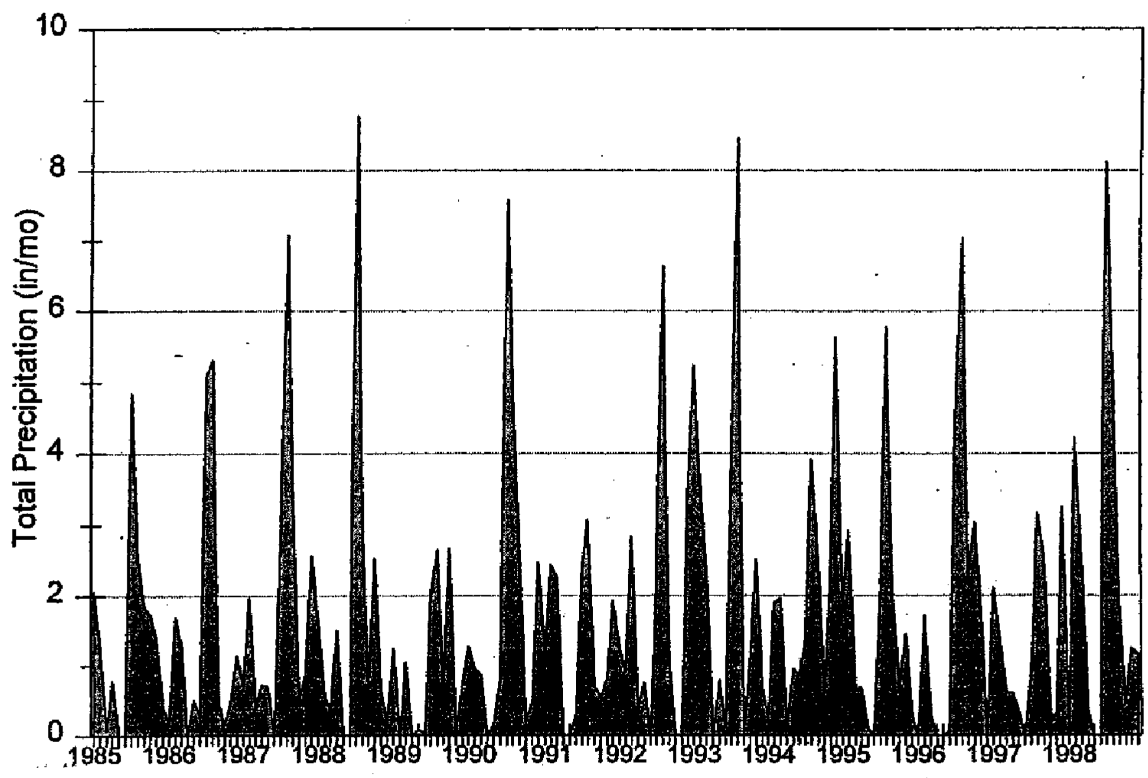


Figure 11. Arivaca Monthly Precipitation, 1985-1998

Runoff Curve Numbers. The direct runoff fraction of precipitation in GWLF is calculated using the curve number method from the SCS TR55 method literature based on land use and soil hydrologic group (SCS, 1986). Curve numbers vary from 25 for undisturbed woodland with good soils, to, in theory, 100, for impervious surfaces. The hydrologic soil group was determined from STATSGO and weighted curve numbers were calculated for each land use category based on soil distribution among hydrologic groups. Curve numbers assigned for the Arivaca watershed are summarized in Table 14.

Table 14. Runoff Curve Numbers for the Arivaca Watershed

Anderson Level 2 Classification	Acres	Curve Number
Evergreen Forest Land	6421.1	88
Urban or Built-Up Land	26.5	96
Shrub and Brush Rangeland	5761.3	90
Cropland and Pasture	420.3	85

Evapotranspiration Cover Coefficients. The portion of rainfall returned to the atmosphere is determined by GWLF based on temperature and the amount of vegetative cover. Cover coefficients were set to 0.8 for the growing season and 0.3 for the nongrowing season. These relatively low numbers reflect the sparse vegetative coverage in the watershed.

Soil Water Capacity. Water stored in soil may evaporate, be transpired by plants, or percolate to ground water below the rooting zone. The amount of water that can be stored in soil—the soil water capacity—varies by soil type and rooting depth. Based on soil water capacities reported in the STATSGO database, soil types present in the watershed, and GWLF user's manual recommendations, the GWLF default soil water capacity of 10 cm was used. Given the low precipitation and high temperatures in the watershed, the capacity is rarely exceeded, and almost all streamflow is simulated as surface runoff. Thus the simulation is insensitive to this parameter.

Recession and Seepage Coefficients. The GWLF model has three subsurface zones: a shallow unsaturated zone, a shallow saturated zone, and a deep aquifer zone. Behavior of the second two stores is controlled by a ground water recession and a seepage coefficient. Because the model simulation yields almost no shallow ground water flow, results are insensitive to specification of these parameters. The recession coefficient was set to 0.15 per day, and the seepage coefficient to 0.

Erosion Parameters

GWLF simulates rural soil erosion using the Universal Soil Loss Equation (USLE). This method has been applied extensively, so parameter values are well established. It computes soil loss per unit area (sheet and rill erosion) at the field scale by

$$A = RE \cdot K \cdot (LS) \cdot C \cdot P$$

where

A = rate of soil loss per unit area,
RE = rainfall erosivity index,
K = soil erodibility factor,
LS = length-slope factor,
C = cover and management factor, and
P = support practice factor.

It should be noted that use of the USLE approach will likely underestimate total sediment yield within a watershed of this type. This is because the USLE addresses only sheet and rill erosion, whereas mass wasting (landslides) and gullying are probably the dominant components of the total sediment budget within the watershed (see NFS, 1973). It was reasoned, however, that the mercury from the watershed that is likely to become bioavailable in the lake would be the mercury associated with the fine sediment fraction. The USLE approach should provide a reasonable approximation of the finer sediment load, even though movement of larger material by other processes is omitted, and can thus serve as a basis for evaluating mercury loading from watershed sediments to the lake.

Soil loss or erosion at the field scale is not equivalent to sediment yield, since substantial trapping may occur, particularly during overland flow or in first-order tributaries or impoundments. GWLF accounts for sediment yield by (1) computing transport capacity of overland flow, and (2) employing a sediment delivery ratio (DR) which accounts for losses to sediment redeposition.

Rainfall Erosivity (RE). Rainfall erosivity accounts for the impact of rainfall on the ground surface, which can make soil more susceptible to erosion and subsequent transport. Precipitation-induced erosion varies with rainfall intensity, which shows different average characteristics according to geographic region. The factor is used in the USLE and is determined in the model as follows:

$$RE_t = 64.6 \cdot a_t \cdot R_t^{\text{[illegible]}}$$

where

RE_t = rainfall erosivity (in megajoules mm/ha-h),
a_t = location- and season-specific factor, and
R_t = rainfall on day t (in cm).

Erosivity was assigned a constant value of 0.3, based on the assumption that values for southern Arizona should be similar to values reported for west and central Texas (Wischmeier and Smith, 1978; Haith and Merrill, 1987).

Soil Erodibility (K) Factor. The soil erodibility factor indicates the propensity of a given soil type to erode, and are a function of soil physical properties and slope. Soil erodibility factors were extracted from the STATSGO soil coverage. Values for individual land use varied from 0.08 for rangeland to 0.19 for forest.

Length-Slope (LS) Factor. Erosion potential varies by slope as well as soil type. Length-slope factors were calculated by measuring representative slopes from topographic maps for upland and bottomland land-use categories. The LS factor is calculated following Wischmeier and Smith (1978):

$$LS = (0.045 \cdot x_\varrho)^{b} \cdot (65.41 \cdot \sin^\theta\phi_\varrho + 4.56 \cdot \sin\phi_\varrho + 0.065)$$

where

ϕ_k = $\tan^{-1}(ps_k/100)$, where ps_k is percent slope
x_k = slope length (m)

Cover and Management (C) and Practice (P) Factors. The mechanism by which soil is eroded from a land area and the amount of soil eroded depend on soil treatment resulting from a combination of land uses (e.g., forestry versus row-cropped agriculture) and the specific manner in which land uses are carried out (e.g., no-till agriculture versus non-contoured row cropping). Land use and management variations are represented by cover and management factors in the USLE and in the erosion model of GWLF. Cover and management factors were drawn from several sources (Wischmeier and Smith, 1978; Haith et al., 1992; Novotny and Chesters, 1981). Cover factors were 0.04 for forest and 0.11 for rangeland, and reflect the relatively sparse cover typical of this landscape. Practice (P) factors were all set to 1, consistent with recommendations for non-agricultural land.

Sediment Delivery Ratio. The sediment delivery ratio (DR) indicates the portion of eroded soil carried to the watershed mouth from land draining to the watershed. The soil can be water-column suspended sediment or bed load, depending on the total size of the subwatershed. Values for DR were estimated from an empirical relationship of DR to watershed area (ASCE, 1975). ASCE's graphical relationship is approximated by the following empirical equation:

$$\mathrm{Log}_{10}(\mathrm{DR}) = -0.301\ \mathrm{Log}_{10}(\mathrm{Area}) - 0.400$$

For lakes, it is not usually appropriate to calculate a DR based on total watershed area since the watershed drains to the lake as a number of smaller, independent watersheds. The sediment delivery ratios were therefore calculated by delineating major subwatersheds for the lake, calculating DR for each, then forming an area-weighted average.

Sediment delivery ratios and K·LS·C·P factors for rural land uses in the Arivaca watershed are summarized in Table 15.

Table 15. Erosion and Sediment Yield Parameters for the Arivaca Watershed Model

Land Use	K	LS	C	P	K·LS·C·P	DR
Rangeland	0.08	5	0.11	1	0.044	0.2
Forest	0.19	0.75	0.04	1	0.0057	0.2

<u>Watershed Model Results</u>: Application of the GWLF model to the period from October 1985 through September yields an average of 11.0 cm/year runoff and 2,520,000 kg sediment yield by sheet and rill erosion. The sediment yield estimate is likely to be less than the actual yield rate from the watershed, as mass wasting loads are not accounted for. As noted above, the mass wasting loads are thought to be of minor significance for loading of bioavailable mercury to the lake. GWLF model results are summarized in Figure 12.

5.5 Watershed Mercury Loading Model

Estimates of watershed mercury loading are based on the sediment loading estimates generated by GWLF through application of a sediment potency factor. A background loading estimate was first calculated, then combined with estimates of loads from individual hot spots.

The majority of the EPA sediment samples showed no clear spatial patterns, with the exception of the "hot spot" area identified at Ruby Dump. Therefore, background loading was calculated using the central tendency of sediment concentrations from all samples excluding Ruby Dump. The background sediment mercury concentrations were assumed to be distributed lognormally, as is typical for environmental concentration samples, and an estimate of the arithmetic mean of

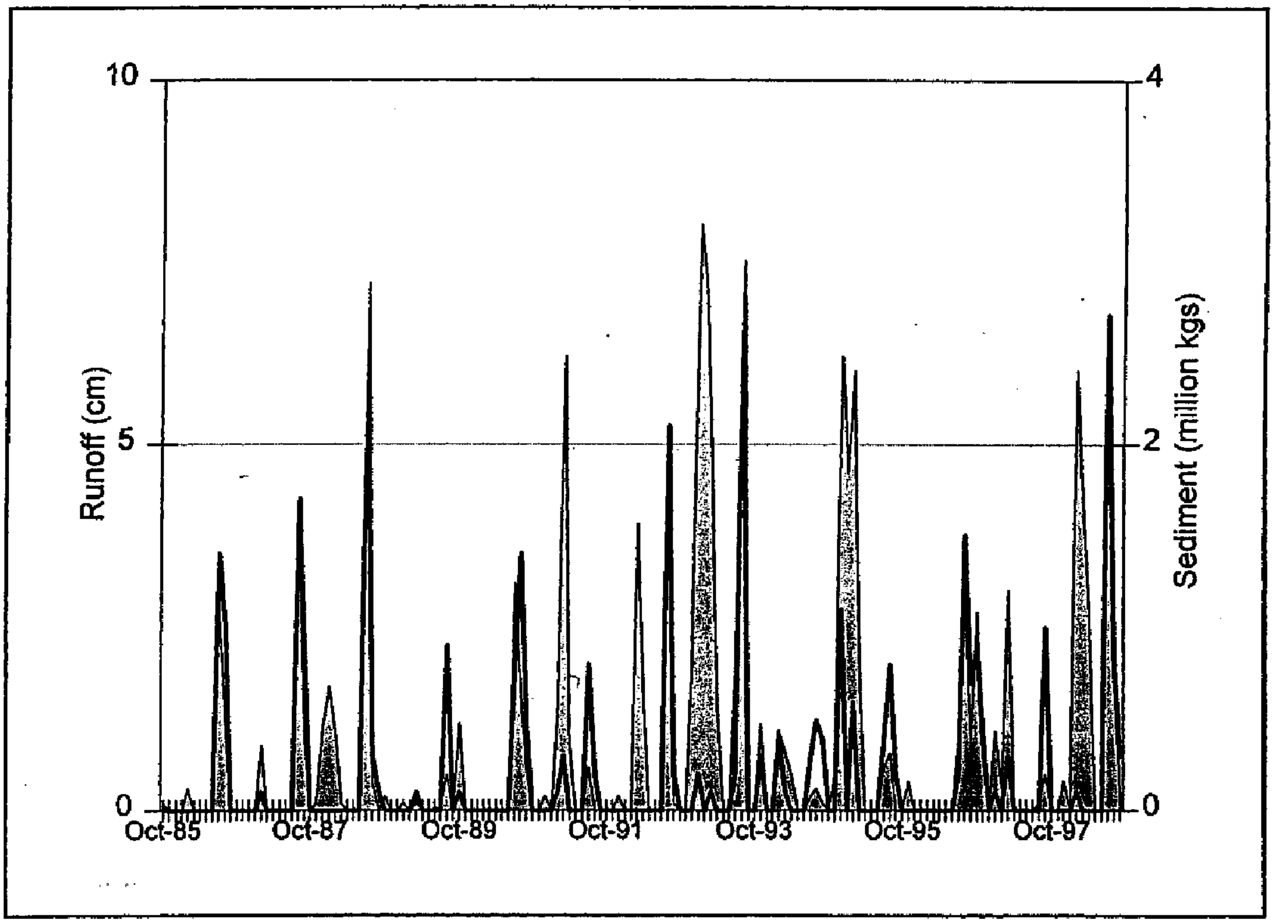


Figure 12. GWLF Watershed Model Predictions for Monthly Runoff (shaded area) and Sediment Yield (heavy line) in Arivaca Lake Waters'ted

70.9 ppb was calculated from the observed geometric mean and coefficient of variation (Gilbert, 1987). Applying this assumption to the GWLF estimates of sediment transport yields an estimated rate of mercury loading from watershed background of 178.9 g/yr. This load is ultimately derived from a combination of atmospheric deposition, naturally occurring mercury in rocks underlying the watershed, and dispersed human activities. For comparison, the estimated rate of gross atmospheric mercury loading to the watershed is 441 g/yr. This gross load exceeds the estimated rate of loading from the watershed to the lake, but is balanced by re-emission to the atmosphere and by infiltration and sequestration in upland soils.

Loading from the Ruby Dump is calculated separately, but is also based on the GWLF estimate of sediment load generated per hectare of "rangeland" (the land use surrounding the hot spots), as reduced by the sediment delivery ratio for the watershed. Sediment load per hectare from the hot spot is assumed to be four times greater than that for normal rangeland, due to the lack of vegetation at the site. This factor is quite uncertain, but its value is not critical to the model results, as revealed by a sensitivity analysis (Table 16).

Table 16. Sensitivity Analysis on the Ruby Dump Sediment Load Multiplier

Sediment Load Multiplier	Percent of Load Attributed to Ruby Dump
1	0.1%
2	0.2%
4	0.4%
8	0.7%

The extent of the "hot spot" was estimated to be 200 feet by 50 feet, based on personal communication from Gregg Olson (U.S. EPA Region 9). The mercury concentration assigned to surface sediments at the dump is the arithmetic average of the four EPA samples taken in October 1997, or 918 ppb.

Based on these assumptions, less than 1 percent of the watershed mercury load to Arivaca Lake appears to originate from Ruby Dump, which is the only identified hot spot in the watershed.

The direct deposition of mercury from the atmosphere onto the Arivaca Lake surface was calculated by multiplying the estimated atmospheric deposition rates (Section 4.3) times the lake surface area.

A similar approach to estimate watershed loads was applied to Peña Blanca Lake (see separate TMDL document) and Patagonia Lake (where no hot spots have been identified). A cross-sectional comparison of watershed mercury loading rates to the three lakes is included in Table 17. Although Patagonia Lake has a higher total annual mercury load, the load per volume of inflow is much lower than those in the two impaired lakes. Atmospheric deposition directly to the lake surface does not appear to be a major source of total mercury load. *Direct* atmospheric deposition onto the lake surface does not appear to be a major source of total mercury load, as it is estimated to account for only about 1 percent of the total annual load to the lake. Atmospheric deposition to the watershed could, however, constitute a significant portion of the net loading from the watershed.

5.6 Lake Hydrologic Model

No monitoring data for inflow, water stage, or outflow are available for Arivaca Lake. The lake level is not actively managed, and releases occur only when storage capacity is exceeded. Therefore, lake hydrology was represented by a simple monthly water balance, using the following assumptions:

1. Inflow from the watershed is given by monthly predictions from the GWLF model application.
2. Direct precipitation on the lake surface is estimated from Arivaca 1E monthly precipitation depth times the lake surface area at the beginning of the month.
3. Evaporation from the lake surface is estimated from pan evaporation data and a pan coefficient of 0.7. This represents the ratio between mean annual lake surface evaporation (Kohler et al., 1959) and average annual evaporation from Class A evaporation pans for this area of southern Arizona (Kohler et al., 1959), and is within the range recommended by Dunne and Leopold (1978).
4. Net gain from or loss to groundwater seepage through the lake bed is assumed to be zero for Arivaca, lacking any evidence to the contrary.
5. Potential storage at the end of the month is calculated as the sum of initial storage plus inflow plus direct precipitation minus evaporation.
6. The stage-area-discharge curve is used to estimate the surface area and elevation of the lake surface corresponding to the potential storage at the end of the month. If the lake surface elevation is computed to be higher than the spillway elevation, the excess volume is assumed to spill downstream.
7. Actual storage at the end of the month is the smaller of potential storage and full-pool storage.
8. Surface area and elevation of the lake surface at the end of the month are updated to reflect actual storage.

Application of the water balance model requires pan evaporation data as an input in addition to the watershed meteorological data described above. As no evaporation data are available at the local Cooperative Summary of the Day meteorological station, pan evaporation data for Tucson were used. Pan evaporation for 1980 through 1995 was obtained from the BASINS 2.0 Region 9 CD-ROM and are summarized in Table 18. Later pan evaporation data were not available for Tucson, so monthly averages were used for the 1996 through 1998 water balance. Use of Tucson data may result in an overestimation of evaporative losses from the lake, since an average pan evaporation rate of 94 inches per year has been reported for the Nogales 6N station at elevation 3,757 feet MSL and south of the Arivaca watershed (NFS, 1973).

Table 17. Watershed Mercury Loading to Arivaca Lake

	Mercury loading to lake (grams per year)			
Water Year	From watershed	From Ruby Dump	From direct atmospheric deposition to lake	Total
1986	170.16	0.65	4.208	175.018
1987	184.34	0.7	4.208	189.248
1988	205.61	0.79	4.208	210.608
1989	70.9	0.27	4.208	75.378
1990	198.52	0.76	4.208	203.488
1991	99.26	0.38	4.208	103.848
1992	163.07	0.62	4.208	167.898
1993	233.97	0.89	4.208	239.068
1994	141.8	0.54	4.208	146.548
1995	219.79	0.84	4.208	224.838
1996	170.16	0.65	4.208	175.018
1997	191.43	0.73	4.208	196.368
1998	276.51	1.06	4.208	281.778
Grand Total	2,325.52	8.88	54.704	2,389.10
Annual Average	**178.89**	**0.68**	**4.21**	**183.78**

Lake Comparison	**Mercury Load (g/yr)**	**Average Inflow (ac-ft/yr)**	**Annual Average Loading/Inflow (g/ac-ft)**
Peña Blanca Lake	193.9	2716	0.071
Arivaca Lake	183.78	3153	0.058
Patagonia Lake	503.24	50926	0.010

The water balance model was run for the period 1985 through 1998. This water balance approach provides a rough approximation of the seasonal cycle of changes in volume and surface area of Arivaca Lake, and of the amount of water released downstream over the spillway. It cannot capture daily or event scale movement of water in and out of the lake. Estimates for individual months are subject to considerable uncertainty in the rainfall-runoff model as well.

Water balance models were also constructed for Peña Blanca Lake and Patagonia Lake. These are similar to the Arivaca application, except that controlled releases from Patagonia Lake are accounted for. Average end-of-month depth for Arivaca is compared to predictions for Peña Blanca and Patagonia Lake in Figure 13.

Table 18. Pan Evaporation Data for Tucson, AZ (inches)

Year	Jan.	Feb.	March	April	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.	*Annual Total*
1980	5.20	6.30	9.20	13.18	15.67	17.81	15.22	13.45	11.40	10.79	7.72	6.93	*132.87*
1981	5.35	6.67	7.95	12.72	14.84	16.88	13.57	15.06	11.78	9.46	7.39	5.73	*127.42*
1982	4.92	5.72	8.18	12.42	15.45	17.30	14.26	12.05	11.41	10.24	5.88	4.36	*122.20*
1983	5.94	5.18	7.73	11.23	16.27	17.16	15.17	12.34	10.48	7.59	5.44	4.72	*119.25*
1984	5.54	7.52	11.52	12.66	16.72	15.65	13.16	11.82	12.24	8.30	6.76	3.93	*125.82*
1985	4.97	5.80	9.16	12.82	15.29	17.75	15.78	13.53	11.39	8.58	5.92	5.15	*126.13*
1986	7.60	6.00	9.69	12.54	16.29	16.89	13.25	12.08	11.95	8.93	5.72	4.05	*124.97*
1987	5.47	6.12	9.31	12.59	13.46	16.49	15.91	12.95	11.32	9.24	6.50	4.32	*123.66*
1988	5.27	6.93	10.91	12.13	17.02	16.65	14.67	12.16	13.23	10.10	7.30	6.49	*132.84*
1989	5.91	7.81	11.91	15.34	17.70	19.13	16.91	14.57	15.04	9.92	7.29	6.20	*147.72*
1990	5.77	6.08	9.63	12.84	15.94	18.41	13.28	12.94	11.44	10.89	7.66	4.99	*129.84*
1991	4.62	6.64	8.08	13.09	16.88	16.23	15.07	12.18	11.24	11.03	6.99	4.54	*126.59*
1992	5.58	5.89	7.88	12.41	13.46	16.41	14.31	11.93	12.68	11.11	7.36	3.66	*122.68*
1993	4.11	4.83	9.09	13.28	16.15	18.18	15.16	11.41	13.12	9.91	6.36	5.47	*127.05*
1994	6.68	6.75	9.56	13.33	14.38	16.63	15.66	13.68	11.53	9.68	6.14	4.66	*128.66*
1995	4.31	6.31	8.89	12.06	14.10	17.25	16.19	12.40	12.61	10.82	6.89	5.58	*127.38*
Ave.	*5.48*	*6.29*	*9.46*	*12.95*	*15.51*	*17.27*	*15.11*	*12.71*	*12.32*	*10.02*	*6.74*	*5.01*	128.87

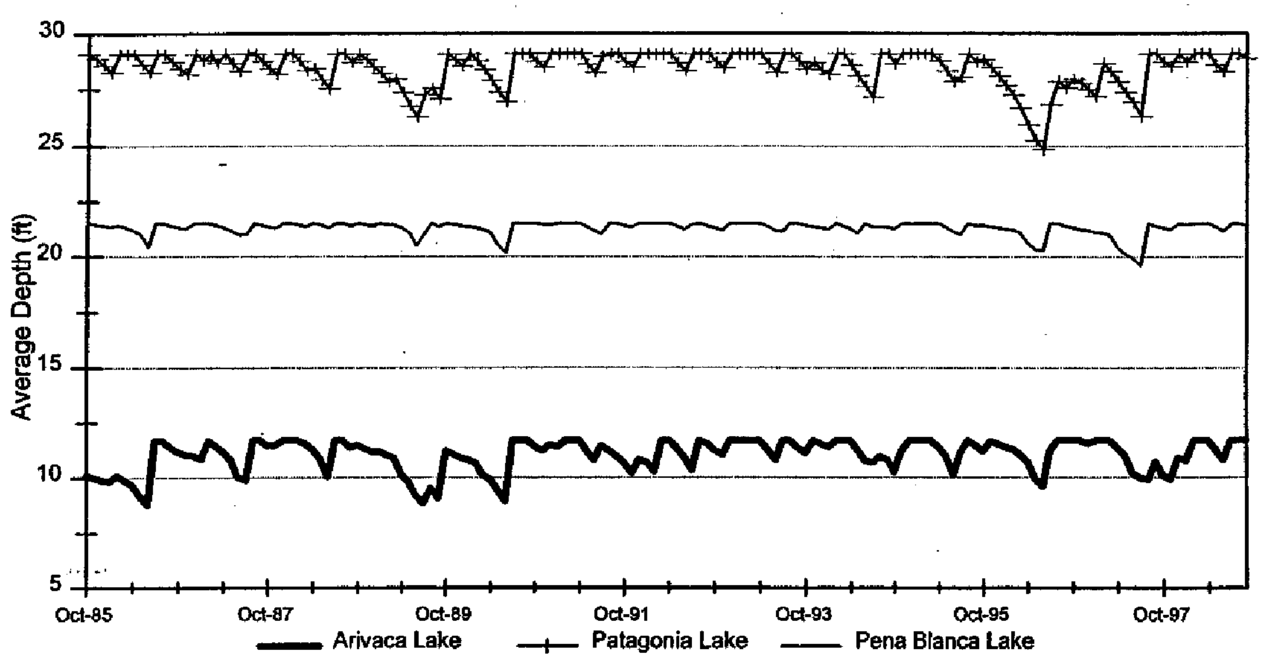


Figure 13. Average Depths (Volume over Surface Area) from Water Balance Model

5.7 Lake Mercury Cycling and Bioaccumulation Model

Cycling and bioaccumulation of mercury within the lake were simulated using the Dynamic Mercury Cycling Model (D-MCM; Tetra Tech, 1999). D-MCM is a Windows 95/NT-based simulation model that predicts the cycling and fate of the major forms of mercury in lakes, including methylmercury, Hg(II), and elemental mercury. D-MCM is a time-dependent mechanistic model, designed to consider the most important physical, chemical, and biological factors affecting fish mercury concentrations in lakes. It can be used to develop and test hypotheses, scope field studies, improve understanding of cause/effect relationships, predict responses to changes in loading, and help design and evaluate mitigation options.

A schematic overview of the major processes in D-MCM is shown in Figure 14. These processes include inflows and outflows (surface and ground water), adsorption/desorption, particulate settling, resuspension and burial, atmospheric deposition, air/water gaseous exchange, industrial mercury sources, in situ transformations (e.g. methylation, demethylation, MeHg photodegradation, Hg(II) reduction), mercury kinetics in plankton, and bioenergetics related to methylmercury fluxes in fish.

Model compartments include the water column, sediments, and a food web that includes three fish populations. Mercury concentrations in the atmosphere are input as boundary conditions to calculate fluxes across the air/water interface (gaseous exchange, wet deposition, dry deposition). Similarly, watershed loadings of Hg(II) and methylmercury are input directly as time-series data. The user provides for hydrologic inputs (surface and ground water flow rates) and associated mercury concentrations, which are combined to determine the watershed mercury loads.

The food web consists of six trophic levels (phytoplankton, zooplankton, benthos, non-piscivorous fish, omnivorous fish, and piscivorous fish). Fish mercury concentrations tend to increase with age, and thus are followed in each year class. Bioenergetics equations for individual fish (Hewitt and Johnson 1992) have been adapted to simulate year classes and entire populations.

The Electric Power Research Institute (EPRI) has funded development of the D-MCM model. It is an extension of previous mercury cycling models developed by Tetra Tech, including the original Macintosh-based MCM models developed during the EPRI-sponsored Mercury in Temperate Lakes Project in Wisconsin (Hudson et al., 1994), and the subsequent steady-state Regional Mercury Cycling Model (R-MCM) (Tetra Tech, 1996). The original model was developed for a set of seven oligotrophic Wisconsin seepage lakes. R-MCM has been applied to 21 lakes in Wisconsin; Lake Barco; Florida; and Lake 240 at the Experimental Lakes Area, Ontario. Performance of the model on the large data sets available for Wisconsin is summarized in Figure 15.

The present version of D-MCM has updated mercury kinetics and an enhanced bioenergetics treatment of the food web. The predictive capability of D-MCM is evolving but is currently limited by some scientific knowledge gaps, which include:

- The true rates and governing factors for methylation and Hg(II) reduction;

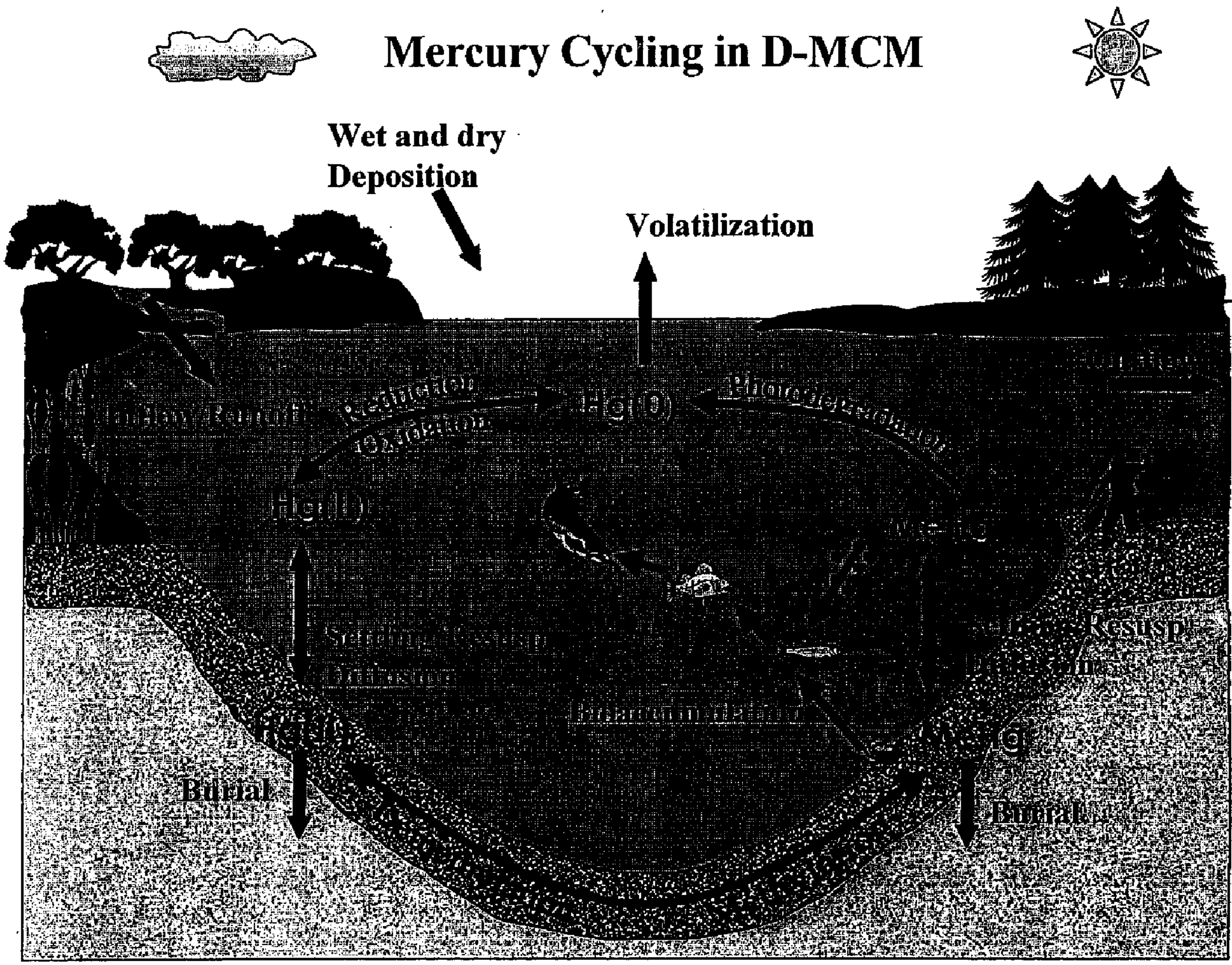


Figure 14. Major Processes in the D-MCM Model

- Factors governing methylmercury uptake at the base of the food web; and
- The effects of anoxia and sulfur cycling.

For example, there is evidence that anoxia and sulfides can affect mercury cycling and influence water column mercury concentrations in lakes (e.g., Benoit et al. 1999 , Driscoll et al. 1994, Gilmour et al. 1998, Watras et al 1994), but the underlying mechanisms and controlling factors have not been quantified.

Another important assumption in the current version of D-MCM is that all of the Hg(II) on particles is readily exchangeable. This results in longer predicted response times for lakes to adjust to changing conditions or mercury loads than likely would occur. It is quite plausible that

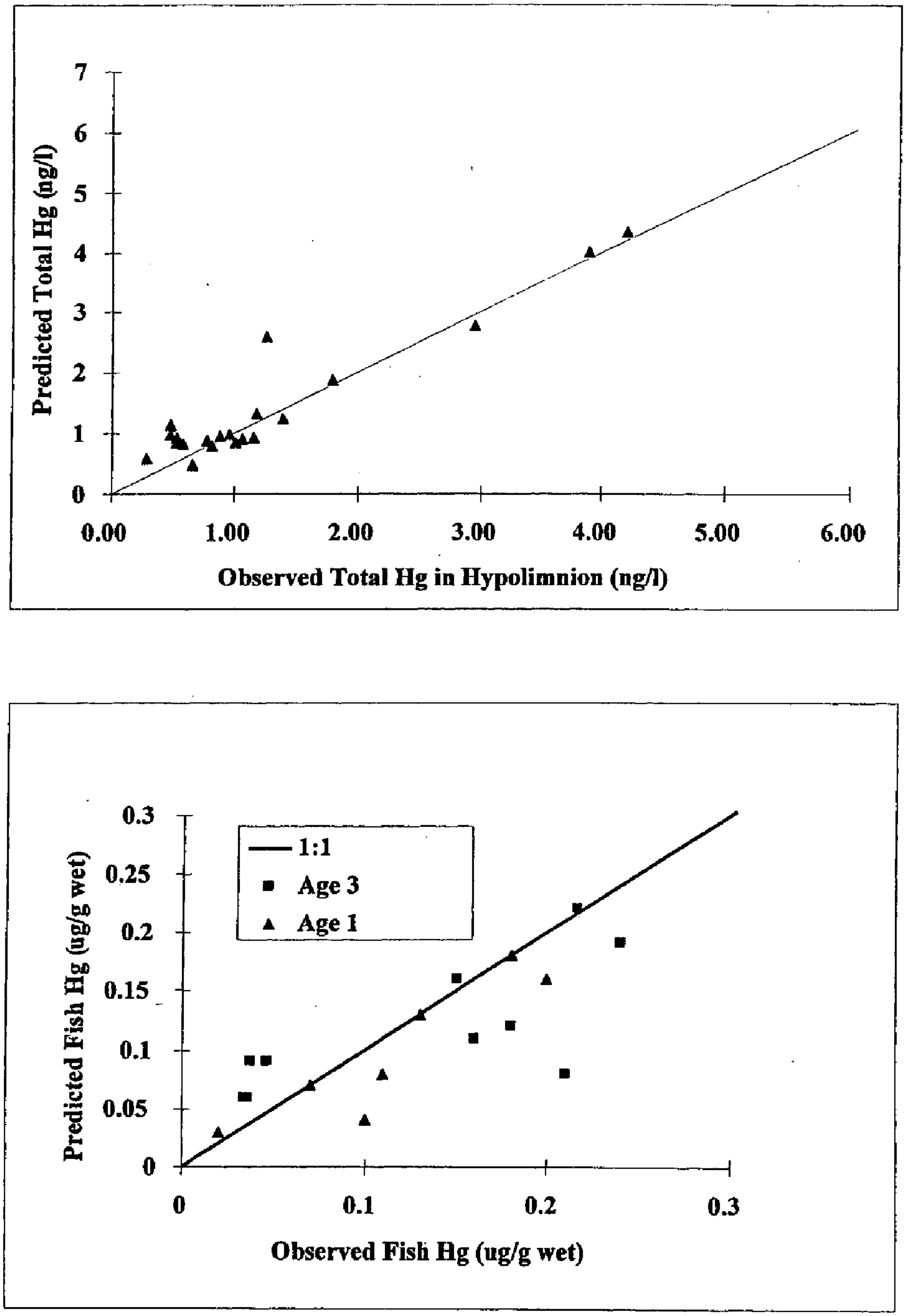


Figure 15. Summary of Mercury Cycling Model Applications to Wisconsin Lakes

a significant fraction of Hg(II) on particles is strongly bound, reducing the pool size of Hg(II) available to participate in mercury cycling and the time required for fish mercury concentrations to adjust to changes in mercury loadings. The magnitude of this error potentially can be quite large for oligotrophic lakes with very low sedimentation rates and very long particulate Hg residence times in the surficial sediments. For systems that have very high sedimentation rates, such as many reservoirs, the practical consequence of this assumption could be quite small. D-MCM modifications are planned in 1999 to include both rapid and slow exchange of Hg(II) on particles. Experimental work is also proposed to develop the associated input values for the model.

Because strong anoxia in the hypolimnion is a prominent feature during summer stratification for the Arizona lakes simulated in this study, D-MCM was modified to explicitly allow significant methylation to occur in the hypolimnion. In previous applications of D-MCM, the occurrence of methylation was restricted to primarily within surficial sediments. That the locus of methylation likely includes or is even largely within the hypolimnion (at least for Arivaca and Peña Blanca lakes) is supported by (1) the detection of significant very high methylmercury concentrations in the hypolimnia of Arivaca and Peña Blanca lakes, and (2) almost complete losses of sulfate in Arivaca Lake in the hypolimnion resulting from sulfate reduction. An input was added to the model to specify the rate constant for hypolimnetic methylation, distinct from sediment methylation.

5.8 Lake Model Application

Model Input Parameters

D-MCM was calibrated to the three study lakes by compiling and inputting into the model data specific to each lake on

- Hydrology and lake physical characteristics (morphometry, stratification);
- External loading rates of mercury (from the atmosphere, watershed, and Ruby Dump);
- Thermodynamic and kinetic rate constants;
- Water and sediment chemistry, and
- Biotic data.

Data specific to each of the three lakes were input into the model first, followed by data derived from calibrations for other lakes where site-specific data were lacking for Arivaca. For instance, thermodynamic and kinetic rate constants specific to Arivaca are not available and were obtained from previous calibrations of D-MCM to lakes in other regions.

Calibration proceeded by running the model with a daily time step for 10 years and adjusting the model so that concentrations of mercury in largemouth bass matched observed averages for each lake. Because the hydrology of these lakes is so dynamic and "flashy," more weight was placed on matching largemouth bass Hg concentrations than on trying to match predicted and observed water chemistry data precisely. This decision was based on the following:

1. Limited water chemistry data that indicate that chemistry in these systems varies rapidly.
2. Hydrologic budgets that show that the hydraulic residence time of all three lakes is relatively short (less than 0.4 years);
3. The lack of truly local atmospheric loading data adequate for resolving and validating short-term dynamics in any of the lakes; and
4. The fact that mercury concentrations in older cohorts of largemouth bass reflect dietary intake throughout their life history and are rather insensitive to short-term variations in water column chemistry and Hg loading dynamics.

The calibrations used the same kinetic (rate constant) assumptions for all three lakes, letting only differences in loading, hydrology, and chemistry dictate differences in response. The following paragraphs give a brief overview of how the input data were assembled and input to the model.

Hydrologic Inputs. D-MCM requires that the user compute all aspects of the hydrologic balance. Inputs include surface water inflow, direct precipitation, surface water outflow, subsurface seepage inflow and outflow, and change in storage. Inputs for all three systems were derived from monthly water balances compiled for October 1985 through September 1998, and computing the average monthly flows during that entire period. An "average" monthly budget was then computed from the hydrologic balance continuity equation, using the computed inflows, precipitation, evaporative losses, and outflow volumes to derive monthly changes in storage. Changes in monthly surface area related to changes in lake volume were computed from hypsographic curves empirically determined for each lake. Looping the monthly inputs for this average year back-to-back resolved discontinuities between the beginning-of-year and end-of-year changes in storage within 2 years. This "resolved" 12-month hydrologic budget was then input into the model.

Atmospheric Inputs. Development of estimates of direct atmospheric input of mercury to the lakes is described in Section 4.3.

Thermodynamic and Kinetic Rate Data. Thermodynamic data and rate kinetics data were derived from previous calibrations performed on multiple lakes in Wisconsin and Lake Barco, a sub-tropical seepage lake in north-central Florida (Hudson et al., 1995; Reed Harris, Tetra Tech, personal communication). Thermal time series data were derived from measured in-lake thermal profiles and from long-term monthly average air temperature measurements measured at Nogales, Arizona, from 1952 through 1998.

Water and Sediment Chemistry Data. Water chemistry from the July 1998 sampling period for chlorine, dissolved organic carbon (DOC), pH, suspended sediment concentrations, dissolved oxygen, and mercury species (particulate and dissolved total mercury and total methylmercury) were used to characterize epilimnetic and hypolimnetic conditions in the model for each lake. Additional data for Arivaca Lake collected during October 1997 were used to establish conditions for Arivaca Lake when the lake is isothermal. Sediment chemistry inputs (total mercury and total organic carbon [TOC]) for the model were developed by computing geometric mean concentrations for samples for each lake measured as a function of location within the lake (epilimnetic vs. hypolimnetic). Although no data were available for porosity and density, it was assumed that the porosities of epilimnetic and hypolimnetic sediments were 0.80 and 0.92, respectively. These values are consistent with porosities often measured in erosional (epilimnetic) and depositional (hypolimnetic) sedimentary environments (cf. Hakanson and Janson, 1983).

Biotic Data. Three trophic levels of fish were simulated in D-MCM: herbivorous fish, omnivorous fish, and piscivorous fish. Because the greatest concentrations of mercury in aquatic food webs develop in piscivorous fish, the focal point of the simulations was on largemouth bass. The rate at which fish feed and grow (bioenergetics) is a critical variable in determining rates of uptake of mercury. For example, all other factors being equal, fish that grow slowly will incorporate higher concentrations of mercury into their tissue than fish that grow more rapidly and efficiently. Measured ages, weights, and lengths from 30 largemouth bass collected in Peña Blanca Lake in May 1995 were used to calibrate age-weight and length-weight relationships. Dietary preferences for each trophic level were based on data developed for the Wisconsin R-MCM lakes.

Calibration

Several assumptions were used to guide the calibrations for the three study lakes. First, it was assumed that there were no good *a priori* reasons to use differing rate or thermodynamic constants for each lake to account for differing mercury behavior. As an example, there may be geochemical differences between the eroded sedimentary material and their ability to adsorb mercury between the Peña Blanca and Arivaca watersheds, but no data are available to substantiate and describe those differences and use of identical values provides a more robust cross-sectional calibration. As a result, binding constants (partition coefficients) for all three lakes were considered identical. A second assumption was that primary locus of methylation was the hypolimnion and that the rates of methylation in each lake were dependent upon the delivery of Hg(II) and the hypolimnetic methylation rate constant. This assumption was invoked after initial simulations that restricted methylation solely to the sediments resulted in severely underpredicted mercury concentrations in biota. This assumption is also consistent with the stable thermal stratification and anoxic conditions that develop in these lakes, the consumption of sulfate observed in Peña Blanca Lake and particularly Arivaca Lake, and the comparatively high concentrations of methylmercury that develop in the hypolimnia and metalimnia of Peña Blanca and Arivaca lakes.

Initial application of D-MCM to Arivaca and Peña Blanca resulted in large overestimates of the amount of mercury predicted in 5-year-old largemouth bass. In a highly parameterized model like D-MCM, a number of possibilities and combinations exist to change rate or thermodynamic constants to yield a more appropriate calibration. However, because the majority of the rate constant and thermodynamic data have been derived from regional calibrations and direct empirical observations from experimental and calibrated lake studies, it was elected not to manipulate any of those parameters to yield a better calibration. First, the particle-Hg(II) partition coefficients were adjusted for particles in the sediment and water column to yield stronger particulate binding, thus reducing the dissolved pool available for methylation. Higher partition coefficients are appropriate for the epilimnion because the hypolimnion becomes seasonally anoxic, which can reduce the ability of inorganic particles to sorb trace elements. Changing the partition coefficient from 5 x 10^{10} m^3/g-particle (dry weight), the value used for Wisconsin and Florida lakes, to a maximum of 1.6 x 10^{12} m^3/g for epilimnetic waters and 5 x 10^{11} m^3/g for hypolimnetic sediments yielded only modest improvements in the calibration.

To further improve the model calibration, focus was placed on one feature of the model known to be potentially inadequate–the ability of the model to predict the amount of labile Hg truly available for desorption. Previous simulations with D-MCM have illustrated that, although initial sorption of Hg to particles may be well characterized by conventional sorption models such as the Freundlich and Langmuir isotherms, desorption of "aged" Hg bound to particles may not follow the same models. In others, some Hg may become irreversibly bound after adsorption has initially occurred, and the amount of mercury ultimately available for desorption is less than the initial sorption models would predict. Stable isotope research to explicitly explore this so-called sorption "hysteresis" phenomenon for watersheds in Canada likely will be conducted in late 1999.

One attractive aspect of this hypothesis is that it could readily explain D-MCM's overprediction of mercury in largemouth bass in both Peña Blanca and Arivaca lakes, which receive the vast majority of their mercury loads through watershed transport of particulates. In calibrating the model to Peña Blanca and Arivaca lakes, it was assumed that the effective loading (i.e., the relative or fractional amount of the load truly available and not irreversibly bound) of mercury from watershed sources in both lakes were equivalent. Loads derived from ball mill tailings at the St. Patrick Mine (Peña Blanca Lake) and from waste disposal at Ruby Dump (Arivaca Lake) were considered wholly available. Using this approach, an effective watershed loading coefficient of 0.62 (i.e., an assumption that 38 percent of the watershed non-point source load is unavailable for desorption) provided very good calibrations for predicted mercury concentrations in largemouth bass (Table 19). Figure 16 presents the temporal dynamics predicted by D-MCM for total Hg(II) and methyl Hg in the hypolimnia and epilimnia of the three study lakes under long-term average conditions. Included in the plots are the results from the July 1997 sampling of the hypolimnia (the only location where both methyl and total mercury were sampled in the water column) for both chemical species. Although the timing of the peak concentrations for the observed and the modeled concentrations do not agree well, the predicted temporal dynamics and ranges in concentrations are quite consistent with the observed values, and the difference in timing very likely reflects the fundamental problem of comparing an "average" year with a single point in time.

Mass balance summaries for inputs, outputs, and internal fluxes in the three lakes are compared in Table 20, expressed in micrograms per square meter of lake surface area. The key difference between Patagonia versus Peña Blanca and Arivaca is in the rate of hypolimnetic methylation. Relationships between mercury concentrations in the various biotic compartments simulated by the model are shown in Figure 17.

After calibration, the model was used to evaluate the load reductions necessary to meet the numeric target. The response of concentrations of mercury in 5-year old largemouth bass to

Table 19. D-MCM Calibration Results for Peña Blanca, Arivaca, and Patagonia Lakes.

Estimates are predicted annual ranges after model has reached steady state. Observed concentrations from July 1997.

Lake	Parameter Type	Methyl Hg (ng/L)	$Hg(II)_{total}$[1] (ng/L)	5-year Largemouth Bass Hg (mg/kg wet)
Pena Blanca	Observed	3.92	11.38	1.42
	Predicted	0.00 – 4.26	0.00 – 17.69	1.40
Arivaca	Observed	14.3	1.46 – 8.3	1.18
	Predicted	0.00 – 12.07	0.00 – 6.28	1.18
Patagonia	Observed	0.78	1.14	0.14
	Predicted	0.00 – 0.12	0.00 – 11.38	0.05

[1]Defined as the difference between measured total $Hg_{unfiltered}$ and $CH_3Hg^{+}_{unfiltered}$.

Table 20. Summary of Average Annual Mercury Fluxes for Peña Blanca, Arivaca, and Patagonia Lakes Predicted by the D-MCM Model. Rates are shown in micrograms per square meter of lake surface area.

	Peña Blanca Lake	Arivaca Lake	Patagonia Lake
Inputs			
Hg(II), Atmosphere	12.4	12.8	12.8
Hg(II), Watershed	193.3	326.3	278.2
Hg(II), Hot Spots	706.8	1.0	0.0
MeHg, Atmosphere	0.02	0.02	0.02
Outputs			
Hg(0), Volatilization	8.8	26.3	11.4
Hg(II), Sediment Burial	809.2	267.7	219.7
Hg(II), Outflow	49.7	9.2	43.4
MeHg, Sediment Burial	36.8	24.1	3.5
MeHg, Outflow	1.0	1.5	0.04
Internal Transformations			
Methylation in Sediment	4.3	7.3	0.7
Methylation in Hypolimnion	43.0	51.8	3.1
Demethylation, Water Column	0.7	2.0	0.006
Demethylation, Sediment	6.1	28.6	0.1
Hg(II) Reduction	4.7	2.1	15.4

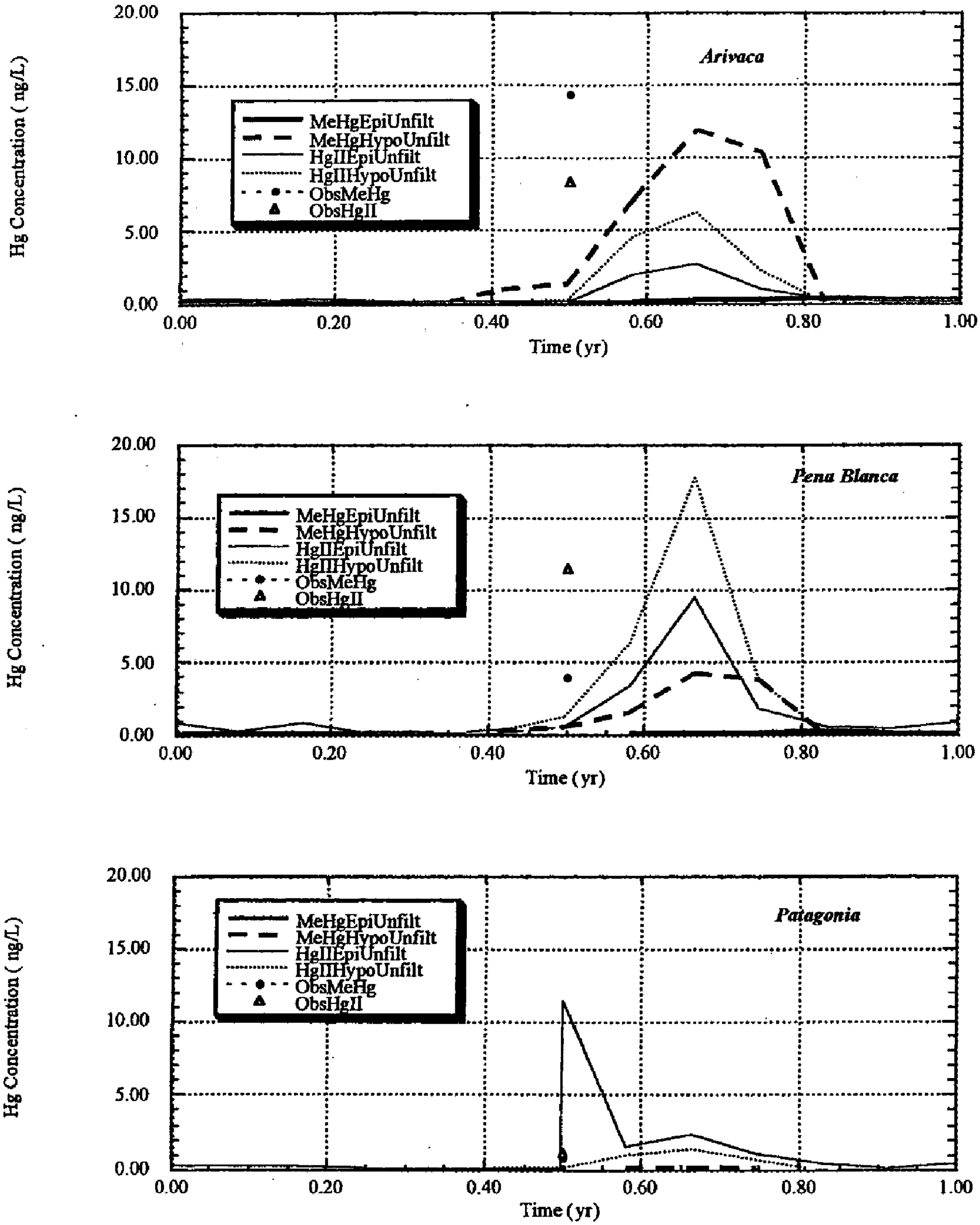


Figure 16. Calibrated D-MCM Predicted Average Annual Dynamics for Unfiltered Concentrations of MeHg and Hg(II) in Peña Blanca, Arivaca, and Patagonia Lakes. Also shown are sampling results from the hypolimnia of all three lakes collected in July 1997.

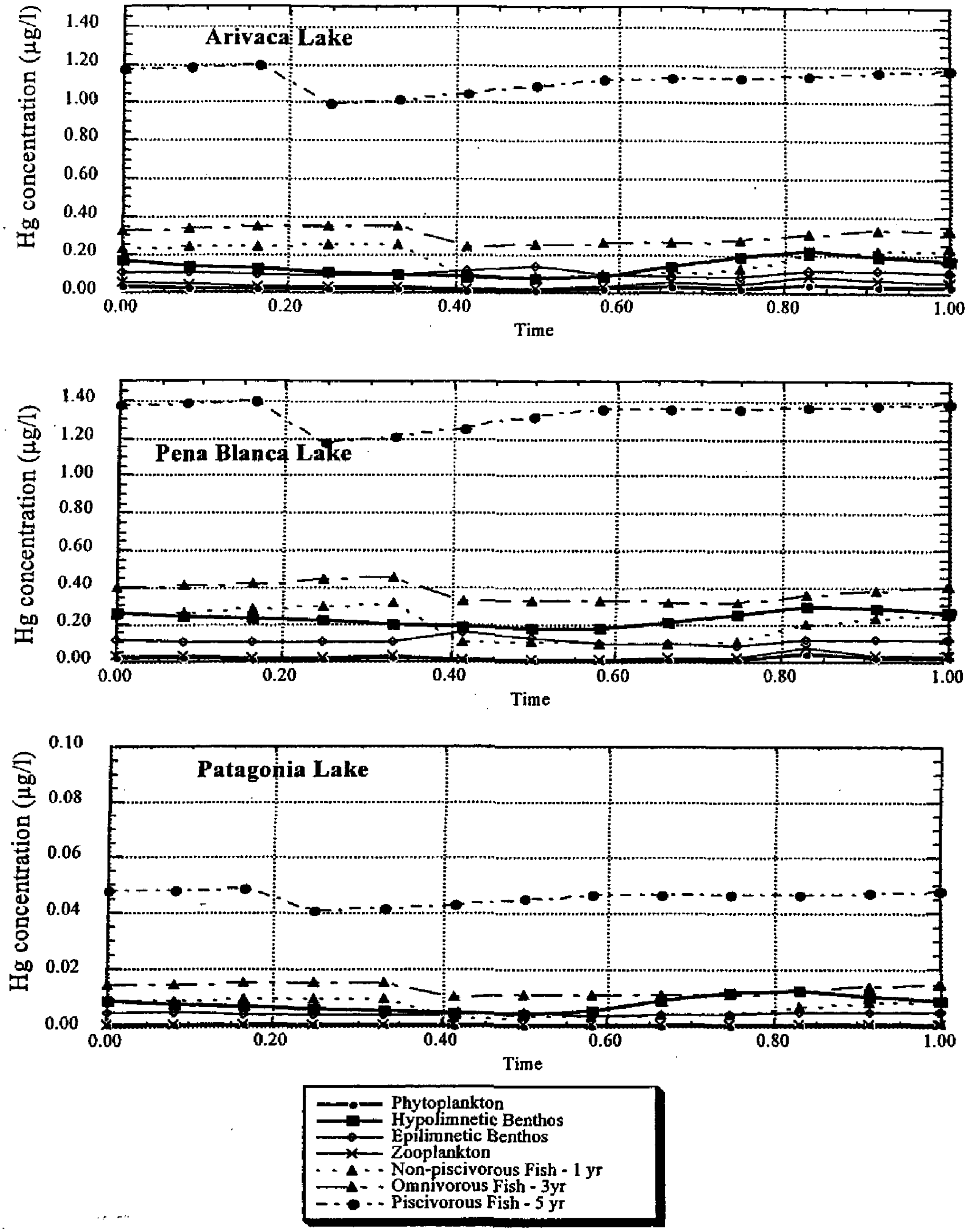


Figure 17. Relationship between Mercury Concentrations in Biotic Compartments Predicted by D-MCM over the Course of a Typical Year

changes in external mercury loads turns out to be nearly linear for these lakes (after a period of several years adjustment), as shown in Figure 18. This is because the sediment burial rates are high, and sediment recycling is low, with the majority of the methylmercury that enters the food chain being created in the anoxic portion of the water column. Figure 18 demonstrates that the numeric target of 1 mg/kg in 5-year old largemouth bass is predicted to be met with a 37 percent reduction in hotspot loads to Peña Blanca Lake, and a 16 percent reduction in total watershed loads to Arivaca Lake (that is, the mercury tissue concentration in 5-year-old largemouth bass is predicted to meet the numeric target of 1 mg/kg when the hot spot load is reduced to 63 percent of current levels for Peña Blanca Lake and the total watershed load is reduced to 84 percent of current levels for Arivaca Lake).

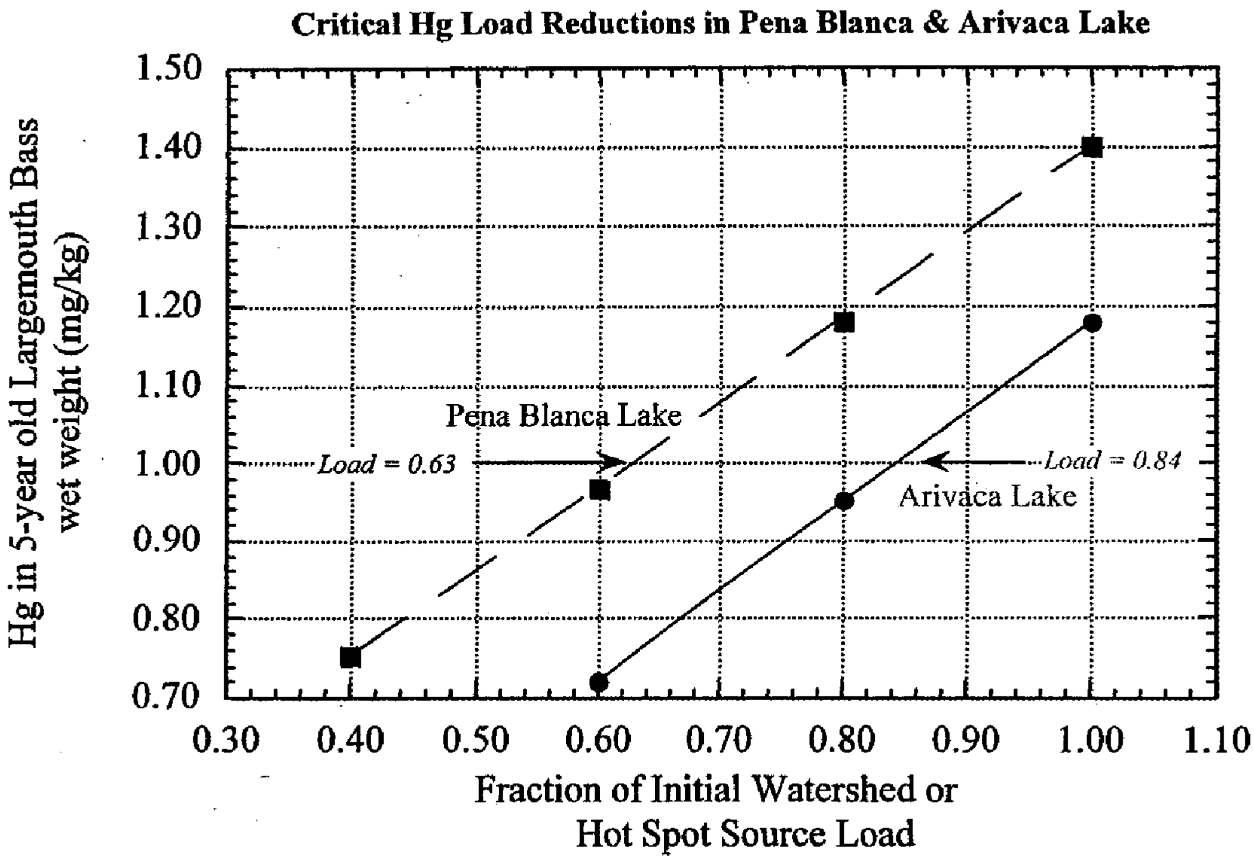


Figure 18. Response of Numeric Target to Reductions in External Mercury Load. Results are shown after approximate stabilization of response. Fractions shown represent fraction of St. Patrick Mine hot spot load for Peña Blanca Lake and fraction of total watershed load for Arivaca Lake.

Model Uncertainties

The model indicates that methylation is largely driven by release of Hg(II) from particles settling into and through the hypolimnion during the summer stratification period when the hypolimnion is anoxic (see Figure 16). Gross (total) loads to Arivaca and Peña Blanca lakes are very similar (see Table 17) and do not wholly account for predicted differences in cycling of mercury. This becomes particularly evident when comparing the average input concentration of mercury to both lakes derived from the total annual load (point source, watershed, and direct atmospheric) and the average total surface water inflow. Critical influent load concentrations (i.e., the maximum allowable load to achieve a target mercury concentration of 1 mg/kg [wet weight] for 5-year-old largemouth bass) for Peña Blanca and Arivaca lakes are 43.2 and 39.8 ng/L, respectively. When corrected for the fraction of the load considered non-reactive, the concentrations are 36.5 and 25.1 ng/L, respectively. This difference is largely due to the large differences in DOC, which is approximately twofold higher in Arivaca (16 to 24 mg/L compared to 9 to 10 mg/L) and which helps promote methylation by providing a source of carbon. The high rates of bacterial metabolism supported by the higher concentrations of DOC also are evidenced by the greater degree of depletion of sulfate in Arivaca Lake. Previous studies on apparent rates of sulfate reduction for lakes in the Upper Midwest and Florida showed that the differences in sulfate losses are related to DOC (Pollman, unpublished data). Uncertainties thus include the actual availability of particulate Hg transported to the lakes and whether rates of methylation would decline significantly if the hypolimnia were precluded from going anoxic.

Other uncertainties include model representation of the role of sulfate reduction and the influence of reduced sulfur species. Because of the large amount of sulfate reduction occurring in Arivaca Lake, the effects of reduced sulfur interacting with Hg(II) (the critical substrate for methylation) and the associated effects on methylation are likely important, but not well understood. For example, the formation of neutral Hg(II) – S^{2-} species might facilitate uptake of Hg(II) by methylating bacteria (Benoit and Gilmour, 1999); conversely, as reduced sulfur concentrations increase, Hg(II) can be sequestered as cinnabar and effectively removed from solution, reducing its availability for methylation.

5.9 Determination of Loading Capacity

A waterbody's loading capacity represents the maximum rate of loading of a pollutant that can be assimilated without violating water quality standards (40 CFR 130.2(f)). Application of the D-MCM lake mercury model provides a best estimate of the loading capacity for mercury of Arivaca Lake of 154.8 grams total mercury per year. This is the maximum rate of loading consistent with meeting the numeric target of 1 mg/kg mercury in 5-year-old largemouth bass.

This estimate of loading capacity is subject to considerable uncertainty, as described in the preceding sections. Uncertainty in the estimation of the loading capacity, and thus the TMDL, is addressed through the assignment of a Margin of Safety (Section 7).

It should also be noted that the loading capacity is not necessarily a fixed number. The numeric target for the TMDL is mercury concentration in fish tissue. This numeric target is linked to external mercury load through a complex series of processes, including methylation/demethylation of mercury and burial of mercury in lake sediments. Any alterations in rates of methylation or in rates of mercury loss to deep sediments will change the relationship between external mercury load and fish tissue concentration and would thus result in a change in the loading capacity for external mercury loads. As discussed in Section 6.7, it may be feasible to increase Arivaca Lake's mercury loading capacity through various lake and watershed management strategies.

6. TMDL, Load Allocations, and Wasteload Allocations

The TMDL and associated allocations are presented in terms of the existing loading capacity of Arivaca Lake, as calculated in Section 5.9.

6.1 Total Maximum Daily Load

The TMDL represents the sum of all individual allocations of portions of the waterbody's loading capacity. Allocations may be made to point sources (wasteload allocations) or nonpoint sources (load allocations) The TMDL (sum of allocations) must be less than or equal to the loading capacity; it is equal to the loading capacity only if the entire loading capacity is allocated. In many cases it is appropriate to hold in reserve a portion of the loading capacity to provide a margin of safety (MOS), as provided for in the TMDL regulation.

Knowledge of mercury sources and the linkage between mercury sources and fish tissue concentrations in Arivaca Lake is subject to many uncertainties at this time. (These uncertainties are discussed in more detail in Section 7). Accordingly, it is appropriate to allocate only a portion of the estimated TMDL at this time. Based on the MOS analysis, an allocation of 75 percent of the loading capacity is proposed in this TMDL study. **The Total Maximum Daily Load for Arivaca Lake is thus a total mercury loading rate of 116.1 g-Hg/yr.**

6.2 Unallocated Reserve

Twenty-five percent of the loading capacity is not being allocated at this time. **Therefore, there is an estimated unallocated reserve of 38.7 g-Hg/yr, designed to provide a Margin of Safety.**

6.3 Load Allocations

Load allocations represent assignment of a portion of the TMDL to nonpoint sources. These allocations must be made even where there is considerable uncertainty about nonpoint loading rates. Federal regulations (40 CFR 130.2(g)) define a load allocation as follows:

> *The portion of a receiving water's loading capacity that is attributed either to one of its existing or future nonpoint sources of pollution or to natural background sources. Load allocations are best estimates of the loading, which may range from reasonably accurate estimates to gross allotments, depending on the availability of data and appropriate techniques for predicting loading. Wherever possible, natural and nonpoint source loads should be distinguished.*

The current state of knowledge of mercury sources in the watershed and transport to the lake requires use of a "gross allotment" approach to the watershed as a whole, rather than assigning individual load allocations to individual tracts or sub-basins within the watershed. Information is currently available to separate sources for load allocations as follows:

- Direct atmospheric deposition onto the lake surface.
- "Hot spot" loading from Ruby Dump.

- Generalized background watershed loading, including mercury derived from parent rock and soil material, small amounts of residual mercury from past mining operations, and the net contribution of atmospheric deposition onto the watershed.

Direct Atmospheric Deposition. Direct deposition to the lake surface is estimated to provide about 4.2 g-Hg per year (Table 17). This amount equals about 2 percent of the estimated total annual mercury loading to the lake. Atmospheric deposition of mercury to Arivaca Lake is believed to derive from long-range transport of global sources. This component is thus: 1) of small significance to the total mercury budget in the lake and 2) not readily controllable. **Because of these two factors, no reduction in existing loads is proposed, and a load allocation of 4.2 g/year is assigned.**

Ruby Dump Site. Ruby Dump is estimated to provide an average annual load of approximately 0.7 g-Hg/yr to Arivaca Lake. Although loads in the past might have been higher, this load is insignificant in light of the total estimated watershed load to the lake. Further, measured concentrations in this area are less than the 35 mg/kg Health-Based Guidance Level (HBGL) promulgated by the Arizona Department of Health Services. **Because of Ruby Dump's small contribution and relatively low soil concentrations, no reduction in the apparent load is proposed for the site and a load allocation of 0.7 g-Hg/yr is proposed.** This allocation might require remedial action if loads from Ruby Dump were found to be higher than estimated in future sampling.

Background Watershed Loading. Background watershed loading appears to be the major source of mercury to Arivaca Lake. As discussed in Section 4, it was infeasible for this analysis to distinguish among different potential sources of mercury loading to the watershed for allocation purposes (with the exception of Ruby Dump. No significant terrestrial sources of mercury were identified during the intensive watershed survey conducted for this TMDL. Regarding air deposition to the watershed land surface, insufficient data were available to to calculate reliable estimates of the proportion of mercury deposited from the air which actually reaches Arivaca Lake. Therefore, a load allocation is being established for overall background watershed loading.

To reduce loads to a level consistent with the proposed TMDL, the background watershed loading allocation is being set at 111.2 g-Hg/yr–a reduction of about 38 percent from existing estimated loads from this source.

6.4 Wasteload Allocations

Wasteload allocations constitute an assignment of a portion of the TMDL to permitted point sources. There are no permitted point source discharges within the Arivaca watershed. Therefore, no wasteload allocations are included in the TMDL and the wasteload allocation is zero.

6.5 Allocation Summary

Proposed allocations for the Arivaca mercury TMDL are summarized in Table 21. These allocations, based on best currently available information, are predicted to result in attainment of acceptable fish tissue concentrations within a time horizon of approximately 10 years. A delay

Table 21. Summary of TMDL Allocations and Needed Load Reductions (in g-Hg/yr)

Source	Allocation	Existing Load	Needed Reduction
Wasteload Allocations	0.0	0.0	0.0
Load Allocations			
Atmospheric Deposition	4.2	4.2	0
Ruby Dump	0.7	0.7	0
Watershed Background	111.2	178.9	67.7
Total	116.1	183.8	67.7
Unallocated Reserve	38.7		
Loading Capacity	154.8		

in achieving standards is unavoidable because time will be required for mercury to cycle through the lake and food chain after loads are reduced.

The current analysis has a significant level of uncertainty, as discussed in Section 7. The proposed allocations are believed to be conservative because an unallocated portion of the TMDL is held in reserve. To provide reasonable assurances that the assigned load allocations will indeed result in compliance with the fish tissue criterion, a continued monitoring and assessment are warranted (see Section 8--Implementation Plan). The purposes of such monitoring will be (1) to evaluate the efficacy of control measures instituted to achieve the needed load reductions and (2) to determine whether the load reductions required by the TMDL lead to attainment of water quality standards. Although estimates of the assimilative capacity and load allocations are based on best available data and incorporate a Margin of Safety, these estimates may potentially need to be revised as additional data are obtained. Because of the uncertainty inherent in the TMDL, continued monitoring is recommended as part of the Implementation Plan for this TMDL..

6.6 Feasibility of Implementing Load Allocations

As discussed in Section 6.3, implementation of the TMDL and associated load allocation will require a significant reduction (about 38 percent) in the watershed loading of mercury. Because of the flashy nature of runoff events, the fact that sediment mercury concentrations appear to be fairly evenly distributed throughout the watershed, and the canyon topography in the Arivaca watershed, it might be difficult to implement sediment control methods that would reduce mercury loads by the required amount.

However, ADEQ and EPA believe the needed levels of mercury load reductions are feasible based on the following considerations:

Potential For Erosion Control

Livestock grazing appears to be the primary land disturbing activity in the watershed. The USFS reports that more than 500 cows graze parts of the Arivaca Lake watershed each year (personal communication with Greg Olsen, EPA, August 16, 1999). Livestock have been identified as an important cause of accelerated erosion rates in many Western watersheds. Reduction of mercury loading from the watershed to Arivaca Lake will probably depend on reduction in sediment erosion rates. Available information indicates that implementation of livestock and range best management practices (BMPs) can reduce erosion rates by about 20-50% (see EPA, 1993; Platts, 1990). For example, a recent nonpoint source demonstration project funded by ADEQ and EPA found that sheet and rill erosion was reduced by an estimated 50% as a result of implementing livestock management practices in the Kanab Creek watershed (ADEQ, 1999). ADEQ and EPA believe significant reductions in erosion rates could be obtained through improved livestock management practices. As a side benefit, implementation of livestock BMPs could result in significant reductions in loadings of DOC and nutrients to the lake. The methyation process appears to be affected by the availability of high levels of DOC and nutrients in the Lake. Reduction of DOC and nutrient levels would be expected to reduce the efficiency of the methylation process at Arivaca Lake, effectively increasing the Lake's mercury loading capacity.

Reductions In Atmospheric Deposition of Mercury

Although reliable estimates are unavailable, new mercury air emissions to the environment appear to be declining. U.S. mercury demand has declined approximately 80% since 1980 (EPA, 1997a). In addition, U.S. mercury emissions have declined significantly since 1990, and are expected to decline further upon implementation of new emission limits on incinerators as required by recent EPA regulations (EPA, 1997a). Global emission trends are less clear, although some data indicate decreasing deposition rates (EPA, 1997a). Reductions in air deposition in Arivaca Lake watershed would eventually result in decreases in mercury loading to the Lake itself.

Potential Location and Remediation of Undiscovered Mercury Sources

Although a fairly extensive investigation of the watershed did not reveal any significant localized sources of mercury in the watershed (with the possible exception of Ruby Dump), ADEQ and EPA believe an additional site investigation is warranted to ensure that no significant sources were missed. If this investigation reveals any significant sources, ADEQ and EPA would work with the USFS or other landowner to ensure that appropriate site remediation is completed. Based on experience with mine site remediation in similar circumstances in Arizona, ADEQ and EPA are confident that newly discovered sites can be effectively eliminated as ongoing mercury sources.

Before any management plan is adopted, it would appear advisable to undertake additional reconnaissance of the watershed to ensure that no mercury hot spots have been overlooked.

6.7 Alternative Management Strategies

As discussed in Section 5.9, an alternative approach to managing the mercury problem in Arivaca Lake would be to increase the loading capacity for mercury. This could be accomplished by any management intervention methods that decreased rates of bacterial methylmercury production within the lake or increased rates of burial and sequestration of mercury in lake sediment. Selection of such an approach would require considerable further research and feasibility studies; the alternative strategies are mentioned here to indicate that a wider range of options than simply reducing external watershed load may be available for achieving support of uses. For Arivaca Lake, no significant point source of mercury has been identified. As discussed above, it appears that a reduction of mercury load to the lake will require a significant reduction in background watershed loading, which might be difficult to achieve. It might, therefore, be desirable to evaluate alternative management strategies that increase the loading capacity of the lake.

Alternative management strategies to increase lake loading capacity for mercury should be regarded as experimental; they do not appear to have been demonstrated at the field scale. Approaches that may be suitable for further investigation include the following:

- **Aeration or Mixing.** Management that reduces the extent and duration of anoxia in the hypolimnion might be useful to reduce rates of mercury methylation. This approach could potentially be implemented either through mechanical mixing to prevent or reduce the period of stratification or through direct aeration of the hypolimnion. Cost and engineering complexity might significantly limit the feasibility of this approach.

- **Sulfur Chemistry Modification.** Altering sulfur chemistry within the lake could potentially increase the rate of precipitation of cinnabar or the activity of demethylating bacteria, thus reducing net rates of methylmercury production. The interactions of sulfur chemistry and lake mercury cycling are incompletely understood at this time, and it is not clear whether practical management options to alter sulfur chemistry exist. Evaluation of this option would require more detailed understanding of chemical and microbial processes within the lake.

- **Alum Treatment.** Treating the lake with alum (aluminum sulfate) should result in the formation of an aluminum hydroxide floc, which would scavenge particulate matter from the water column as it settles and form a barrier to solute exchange across the sediment-water interface. This is an approach sometimes used to manage eutrophication due to excessive phosphorus concentrations. Alum treatment could potentially reduce the mercury available for methylation within the system, as well as reducing methylmercury recycling from the sediments. Additional investigations would need to be pursued to determine (1) whether removal of particulate mercury by alum flocculation would indeed result in a sufficient reduction in methylmercury production and recycling to attain standards; (2) the cost and feasibility of alum treatment sufficient to ensure a stable floc in the presence of relatively high dissolved organic carbon levels; and (3) the potential for lowering the pH of the lake and creating a risk of aluminum toxicity.

- **Reduction of DOC and Nutrient Levels.** One of the ways in which Arivaca Lake appears to differ from the other two lakes is in having higher DOC concentrations. High DOC is believed to help promote methylation by providing a source of organic carbon. Thus control of DOC levels, which are at least in part correlated to in-lake algal and macrophyte productivity, may be worth investigating as a means to control mercury methylation. Arivaca also differs from Peña Blanca in having 3 percent of the watershed land area in pasture (Peña Blanca has no pasture, and Patagonia has less than 1 percent of its watershed area in cropland and pasture). The presence of approximately 500 cattle in the watershed probably contributes to higher DOC concentrations, both through direct loading of organic wastes and through increased nutrient loading that supports algal growth in the lake. It may thus be worth some further investigation to determine the impacts of improved livestock management on water chemistry and mercury cycling within the lake.

- **Dredging of Lake Sediments.** Although this approach should be considered a worst case option, actual removal of mercury contaminated sediments could reduce the problem of bioaccumulation in the food chain. In the future, it may prove necessary to dredge the lake in order to maintain reservoir capacity. This approach would need to be carefully evaluated to ensure that it does more good than harm to the Lake's fish population.

7. Margin of Safety, Seasonal Variations, and Critical Conditions

7.1 Sources of Uncertainty

The analysis for the draft Arivaca TMDL contains numerous sources of uncertainty, and load allocations must be proposed as best estimate "gross allotments," in keeping with the TMDL regulation at 40 CFR 130.2(g). Key areas of uncertainty have been highlighted in the Source Assessment and Linkage Analysis sections, and are summarized below.

The sources of uncertainty can be divided into two groups. The first group consists of sources of uncertainty that directly affect the ability of the linkage analysis to relate the numeric target fish tissue concentration to external mercury loads. These sources of uncertainty propagate directly to uncertainty in estimation of the loading capacity and TMDL. The second group consists of uncertainty in the estimation of external loads. These have their primary impact on allocations and impact the estimation of loading capacity only indirectly, by causing a potential mis-specification in the data used for lake model calibration. The loading capacity estimate is much more sensitive to uncertainty in the first group, and relatively robust to uncertainty in the second group.

The first group includes the following:

- Hydraulic response of the lake, including rate of flushing downstream, is estimated from crude water balance calculations. The reduction in volume of the lake by sedimentation over time since impoundment is unknown and both the current morphometry of the lake and actual rates of outflow are uncertain at this time.
- A key uncertainty of the D-MCM application is the actual availability of particulate mercury transported into the lakes.
- The role of sulfate reduction and the influence of reduced sulfur species on mercury cycling within the lakes is not well understood.
- It is suggested that rates of mercury methylation in the hypolimnion would decline if the hypolimnion was precluded from going anoxic; however, the exact impact is uncertain.

The second group includes the following:

- Watershed background loading of mercury is estimated using a simple water balance/sediment yield model. While the concentrations in tributary sediments are based on measured data, the estimated actual rates of movement of this sediment to the lake are not constrained by field measurements at this time.
- Estimates of atmospheric wet deposition of mercury are based on the MDN station at Caballo, New Mexico, which has only a limited period of record and is several hundred miles removed from the Peña Blanca watershed. Net dry deposition is assumed to be roughly equal to wet deposition, without direct evidence from the watershed. Total mercury deposition to the watershed may well differ from the estimates used by a factor of 3 or more, based on best professional judgement of the authors. Such uncertainty will,

however, have only a minor effect on the estimates of total external mercury loads because direct deposition to the lake is a minor component of the total mercury loading budget and atmospheric loading onto the watershed land surface is combined within the data-based estimated of net mercury loading from the watershed and not estimated from deposition data.

Quantitative estimates have been made for only some of these sources of uncertainty. It is also not appropriate to assume that all the sources of uncertainty are additive, since some sources will have positive or negative correlations with other sources. A full, quantitative analysis of uncertainty in the TMDL has not yet been feasible, but might be appropriate as additional data are collected. The best professional judgment of the authors is, however, that there is a high probability that the true loading capacity of Arivaca Lake lies within plus or minus 25 percent of the best estimate of 154.8 g-Hg/yr.

The uncertainty in the estimation of loading capacity and the TMDL could be reduced directly through collection of additional data to better characterize external loading rates, internal stores of mercury, and year-to-year variability in lake response. Uncertainty in the D-MCM modeling of mercury cycling within the lake could also be reduced through the following efforts:

- Collecting higher-frequency data on thermal stratification and water chemistry within the lake, including mercury species, pH, chlorine, DOC, sulfur species, and particulate concentrations.
- Obtaining better characterization of the particulate matter in the study lakes, including settling velocity and mercury sorption characteristics.
- Developing more information on sulfate reduction and the production of reduced sulfur species in pore water and the hypolimnion. Improved thermodynamic data on sulfur-Hg(II) interactions are also needed.
- Obtaining better understanding as to which Hg(II) species are most readily taken up by methylating bacteria and the rates at which uptake occurs.

7.2 Margin of Safety

All TMDLs are required to include a Margin of Safety to account for uncertainty in the understanding of the relationship between pollutant discharges and water quality impacts. The Margin of Safety may be provided explicitly through an unallocated reserve or implicitly through use of adequately conservative assumptions in the analysis.

This proposed TMDL incorporates an explicit Margin of Safety as an unallocated reserve equal to 25 percent of the estimated loading capacity. As described in Section 7.1, the margin of uncertainty about the estimated loading capacity is believed to be plus or minus 25 percent.

In sum, the proposed TMDL incorporates a reasonable Margin of Safety that is believed to account for uncertainty in the understanding of the relationship between pollutant discharges and water quality impacts. It is not, however, possible at this time to precisely estimate the magnitude of uncertainty in the estimation of lake loading capacity. As a result, there is some small, but non-zero potential risk that the proposed allocations will not achieve water quality standards. Continued monitoring and adaptive management should be part of any Management Plan for Arivaca Lake.

7.3 Seasonal Variations and Critical Conditions

The TMDL is estimated to address fish tissue concentrations associated with bioaccumulation of mercury within Arivaca Lake, and there is no evidence of excursions of water quality standards for mercury. Because methylmercury is a bioaccumulating toxin, concentrations in tissue of game fish integrate exposure over a number of years. As a result, annual mercury loading is more important for the attainment of standards than instantaneous or daily concentrations, and the TMDL is written in terms of annual loads. It is not necessary to address standard wasteload allocation critical conditions, such as concentrations under 7Q10 flow, because it is loading, rather than instantaneous concentration, that is linked to impairment.

The impact of seasonal and other short-term variability in loading is damped out by the biotic response. The numeric target selected is tissue concentration in 5-year-old bass, which represents an integration over several years of exposure, suggesting that annual rather than seasonal limits are appropriate. Nonetheless, the occurrence of loading which impacts fish does involve seasonal components. First, loading, which is caused by infrequent major washoff events in the watershed, is highly seasonal in nature, with most loading occurring during the July–August wet period. Second, bacterially mediated methylation of mercury is also likely to vary seasonally. The timing of washoff events is not amenable to management intervention. Therefore, it is most important to control average net annual loading, rather than establishing seasonal limits, in calculating the TMDL consistent with the existing loading capacity. There may, however, be a potential for modifying the seasonal cycle of bacterial methylation through management intervention, as discussed above in Section 6.7.

8. Implementation Plan

This plan identifies followup implementation actions and monitoring activities which are needed to ensure that the TMDL and associated allocations are attained. The plan is explained in Table 22 which identifies actions, timeframes, and potentially responsible parties.

Table 22. Arivaca Lake TMDL Implementation Plan

Action	Timeframe For Implementation	Potential Responsibile Party
1. Supplemental Watershed Investigation – walk all main tributaries Lake not previously investigated by ADEQ or EPA – identify locations of mine-related operations, refuse dumps, or other sites which might be mercury sources – collect sediment samples upstream, downstream, and at the identified locations for mercury analysis – if monitoring data for identified sites indicates sites are significant sources of mercury, implement remedial actions to address mercury loading causes	1999-2000	ADEQ EPA USFS
2. Livestock BMP Improvements – review existing grazing permits and associated livestock BMPs currently in place – identify potentially effective livestock BMPs and implementation mechanisms – if necessary, work with permit holder(s) and USFS to make BMP improvements a permit requirement – monitor BMP installation and effectiveness	2000	ADEQ USFS permit holder(s)

(Continued on next page)

Action	Timeframe For Implementation	Potential Responsibile Party
3. Fish Tissue Monitoring – develop ongoing fish tissue monitoring plan – collect and test fish for mercury according to plan, beginning in 2003 – evaluate results and consider whether adequate progress toward attainment of TMDL is being made – if adequate progress is being made, continue periodic tissue monitoring – if adequate progress not being made, revise monitoring plan, potentially considering air deposition and sediment monitoring and further characterization of Ruby Dump and other identified sources (if any)	beginning 1999, ongoing	ADEQ AZGF
4. TMDL Review and Revision – review TMDL progress consistent with monitoring plan – revised TMDL and implementation plan as necessary	every 4-5 years	ADEQ EPA

9. References

Adriano, D.C. 1986. *Trace Elements in the Terrestrial Environment.* Springer-Verlag, New York.

Aitchison, J., and J.A.C. Brown. 1969. *The Lognormal Distribution.* Cambridge University Press, Cambridge, England.

Anderson, J.R., E.E. Hardy, J.T. Roach, and R.E. Witmer. 1976. A Land Use and Land Cover Classification for Use with Remote Sensor Data. U.S. Geological Survey Professional Paper 964. U.S. Geological Survey, Reston, VA.

Arizona Department of Environmental Quality. 1999. 319(h) Projects, FY 1990 - Present. Phoenix, AZ.

ASCE. 1975. *Sedimentation Engineering*, ed. V.A. Vanoni. American Society of Civil Engineers, New York.

Benoit, J.M., C.C. Gilmour, R.P. Mason and A. Heyes. 1999. Sulfide controls on mercury speciation and bioavailability to methylating bacteria in sediment pore waters. *Environmental Science and Technology* 33(6): 951-957.

Burke, J., M. Hoyer, G. Keeler and T. Scherbatskoy. 1995. Wet deposition of mercury and ambient mercury concentrations at a site in the Lake Champlain basin. *Water, Air, and Soil Pollution* 80:353-362.

Delfino, J.J., B.E. Rood, J.M. Andres, Jr., and C.D.A Earle. 1994. Mercury Spatial Heterogeneity in Everglades Soil Cores and a Comparison of Mercury Accumulation in Wetlands and Associated Lakes. Final Project Report, Volume 1. Florida Department of Environmental Protection, Tallahassee, FL.

Driscoll, C.T., C. Yan, C.L. Schofield, R. Munson, and J. Holsapple. 1994. The mercury cycle and fish in the Adirondack lakes. *Environmental Science and Technology* 28(3): 136a-143a.

Dunne, T., and L.B. Leopold. 1978. *Water in Environmental Planning.* W.H. Freeman and Co., San Francisco.

Gilbert, R.O. 1987. *Statistical Methods for Environmental Pollution Monitoring.* Van Nostrand Reinhold, New York.

Gilmour, C.C., G.S. Riedel, M.C. Ederington, J.T. Bell, J.M. Benoit, G.A. Gill, and M.C. Stordal. 1998. Methylmercury concentrations and production rates across a trophic gradient in the northern Everglades. *Biogeochemistry* 40 (2/3): 327-345.

Håkanson, L., and M. Janson. 1983. *Principles of Lake Sedimentology.* Springer-Verlag, Berlin.

Haith, D.A., R. Mandel, and R.S. Wu. 1992. *GWLF, Generalized Watershed Loading Functions, Version 2.0, User's Manual.* Dept. of Agricultural and Biological Engineering, Cornell University, Ithaca, NY.

Haith, D.A., and D.E. Merrill. 1987. Evaluation of a daily rainfall erosivity model. *Transactions of the American Society of Agricultural Engineers* 30(1): 90-93.

Hewitt and Johnson. 1992. Fish Bioenergetics Model 2. WIS-SG-91-250. University of Wisconsin Sea Grant Institute.

Hudson, R.J.M., S.A. Gherini, C.J. Watras, and D.B. Porcella. 1994. Modeling the biogeochemical cycle of mercury in lakes: The Mercury Cycling Model (MCM) and its application to the MCL study lakes. In *Mercury as a Global Pollutant,* ed. C.J. Watras and J.W. Huckabee, pp. 475-523. Lewis Publishers, Chelsea, MI.

Keeler, G.J,, M.E. Hoyer, and C.H. Lamborg. 1994. Measurements of atmospheric mercury in the Great Lakes Basin. In *Mercury as a Global Pollutant,* ed. C.J. Watras and J.W. Huckabee, pp. 231-241. Lewis Publishers, Chelsea, MI.

Keith, S.B. 1975. Index of Mining Properties in Santa Cruz County, Arizona. Geological Survey Branch Bulletin 191. Arizona Bureau of Geology and Mineral Technology.

Kohler, M.A., T.J. Nordenson, and D.R. Baker. 1959. Evaporation Maps for the United States. U.S. Weather Bureau Technical Paper 37.

Lahlou, M., L. Shoemaker, S. Choudhury, R. Elmer, A. Hu, H. Manguerra, and A. Parker. 1998. *Better Assessment Science Integrating Point and Nonpoint Sources, BASINS Version 2.0, User's Manual.* EPA-823-B-88-006. Office of Water, U.S. Environmental Protection Agency, Washington, DC.

Lechler, P.J. 1998. Modern mercury contamination from historic amalgamation milling of silver-gold ores in the Carson River, Nevada and Jordan Creek, Idaho: importance of speciation analysis in understanding the source, mobility, and fate of polluted materials. In *Mercury Contaminated Sites: Characterization, Risk Assessment, and Remediation,* ed. R. Ebinghaus et al., pp. 337-355. Springer-Verlag, Berlin.

Lindberg, S.E., R.R. Turner, T.P. Meyers, G.E. Taylor Jr., and W.H. Schroeder. Atmospheric concentrations and deposition of Hg to a deciduous forest at Walker Branch watershed, Tennessee, USA. *Water, Air, and Soil Pollution* 56: 577-594.

Lindqvist, O., K. Johansson, M. Aastrup, A. Andersson, L. Bringmark, G. Hovsenius, L. Hakanson, A. Iverfeldt, M. Meili, and B. Timm. 1991. *Mercury in the Swedish Environment: Recent Research on Causes, Consequences, and Corrective Methods.* Kluwer Academic Publishers, Dordrecht, Netherlands.

Mitchell, D. 1995a. Arivaca Lake Creel Survey 1994. Statewide Fisheries Investigations, Survey of Aquatic Resources, Federal Aid Project F-7-M-37. Arizona Game and Fish Department, Phoenix, AZ.

Mitchell, D. 1995b. Arivaca Lake Spring 1995 Aquatic Wildlife Survey. Statewide Fisheries Investigations, Survey of Aquatic Resources, Federal Aid Project F-7-M-38. Arizona Game and Fish Department, Phoenix, AZ.

NFS. 1973. Erosion and Sediment Yield, Peña Blanca Watershed, Coronado National Forest. National Forest Service, Southwestern Region.

Novotny, V., and G. Chesters. 1981. *Handbook of Nonpoint Pollution.* Van Nostrand Reinhold, New York.

Platts, W.S. 1990. Managing Fisheries and Wildlife on Rangelands Grazed by Livestock. Nevada Department of Wildlife. Carson City, NV.

Popp, C.J., D.K.Brandvold, K. Kirk, L.A. Brandvold, V. McLemore, S. Hansen, R. Radtke, and P. Kyle. 1996. *Reconnaissance and Investigation of Trace Metal Sources, Sinks, and Transport in the Upper Pecos River Basin, New Mexico.* Cooperative Agreement No. 3-FC-40-13830. New Mexico Institute of Mining and Technology, U.S. Department of the Interior and U.S. Bureau of Reclamation.

SCS. 1986. *Urban Hydrology for Small Watersheds.* Technical Release No. 55 (second edition). Soil Conservation Service, U.S. Department of Agriculture, Washington, DC.

Sigler, S.A. 1998. The History of Mercury Sedimentation in a Florida Seepage Lake. M.S. Thesis, Florida State University, Tallahassee, FL.

Tetra Tech. 1996. Regional Mercury Cycling Model: A Model for Mercury Cycling in Lakes (R-MCM Version 1.0b Beta), Draft User's Guide and Technical Reference. Electric Power Research Institute, Palo Alto, CA.

Tetra Tech. 1999. Dynamic Mercury Cycling Model for Windows 95/NT™, A Model for Mercury Cycling in Lakes, D-MCM Version 1.0, User's Guide and Technical Reference. Electric Power Research Institute, Palo Alto, CA.

U.S. EPA 1993. *Guidance Specifying Management Measures For Sources of Nonpoint Pollution In Coastal Waters*, EPA 840-B-92-002. Office of Water, U.S. Environmental Protection Agency, Washington, D.C.

U.S. EPA. 1995. *Guidance for Assessing Chemical Contaminant Data for Use in Fish Advisories,* Volume 1, *Fish Sampling and Analysis.* Second Edition. EPA 823-R-95-007. Office of Water, U.S. Environmental Protection Agency, Washington, DC.

U.S. EPA . 1997a. *Mercury Study Report to Congress,* Volume 2, *An Inventory of Anthropogenic Mercury Emissions in the United States.* EPA-452-R/97-004. U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards and Office of Research and Development, Washington, DC.

U.S. EPA. 1997b. *Mercury Study Report to Congress,* Volume 3: *Fate and Transport of Mercury in the Environment.* EPA-452-R/97-005. U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards and Office of Research and Development, Washington, DC.

U.S. EPA 1997c. *Guidance for Assessing Chemical Contaminant Data for Use in Fish Advisories,* Volume 2, *Risk Assessment and Fish Consumption Limits.* Second Edition. EPA 823-B-97-009. Office of Water, U.S. Environmental Protection Agency, Washington, DC.

USGS. 1990. USGeoData 1:250,000 and 1:100,000 Scale Land Use and Land Cover and Associated Maps Digital Data. U.S. Geological Survey, Reston, VA.

Watras, C.J., N.S. Bloom, R.J.M. Hudson, S. Gherini, R. Munson, S.A. Claas, K.A. Morrison, J. Hurley, J.G. Wiener, W.F. Fitzgerald, R. Mason, G. Vandal, D. Powell, R. Rada, L. Rislov, M. Winfrey, J. Elder, D. Krabbenhoft, A.W. Andren, C. Babiarz, D.B. Porcella, and J.W. Huckabee. 1994. Sources and fates of mercury and methylmercury in Wisconsin lakes. In *Mercury Pollution: Integration and Synthesis,* ed. C.J. Watras and J.W. Huckabee. Lewis Publishers, Chelsea, MI.

Wischmeier, W.H., and D.D. Smith. 1978. *Predicting Rainfall Erosion Losses: A Guide to Conservation Planning.* Agricultural Handbook 537. U.S. Department of Agriculture, Washington, DC.